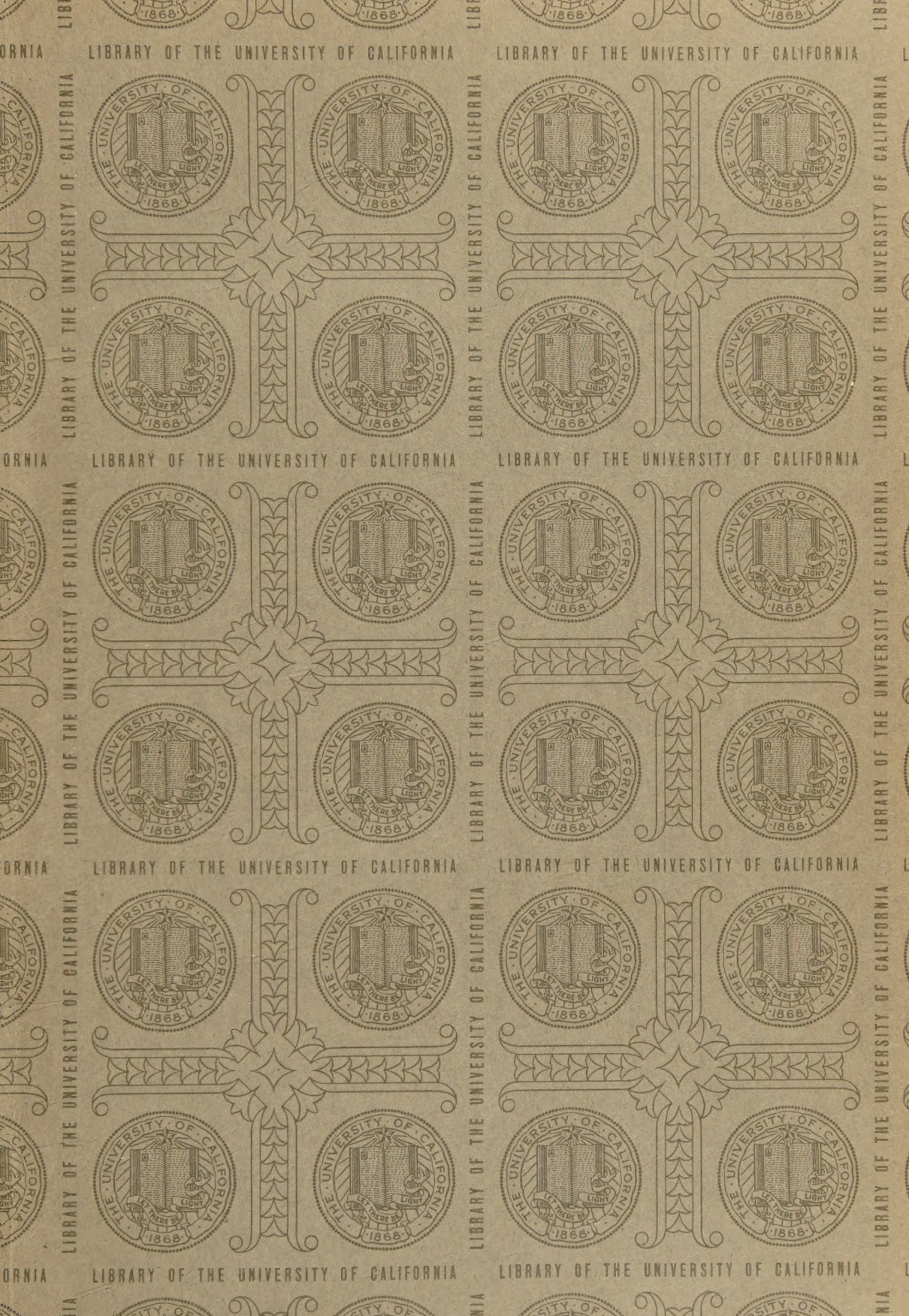


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REPORT ON RADIATION
AND THE
QUANTUM-THEORY.

BY
J. H. JEANS.

SECOND EDITION.

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PREFACE TO THE SECOND EDITION.

When the first edition of this report was written in 1914, the Quantum-Theory was but little understood in this country, and in so far as it was understood, was an object of suspicion to most physicists. These considerations determined the form assumed by the original report; it had to be an *apologia* as well as an exposition.

In preparing a second edition I have retained the arrangement and the main bulk of the old report. Such omissions as have been made have been prompted by the feeling that the Quantum-Theory need no longer be considered on the defensive; the additions, which are much more numerous than the omissions, represent merely the filling in of the old framework which has been necessitated by the rapid growth of the theory.

No attempt has been made to expand the report into a complete treatise—nothing less than ten times the space available would have sufficed for this. In particular, I have been content to treat questions of atomic structure and spectral lines only in the very broadest way; the recent English translation of Sommerfeld's "Atombau und Spektrallinien" would have made any detailed treatment of these questions in the present report superfluous.

I am indebted to Dr. D. Owen for help in reading the proofs and for the preparation of the index which accompanies the report.

J. H. JEANS.

CONTENTS.

CHAPTER	PAGE
I.—INTRODUCTORY: ON THE NEED FOR A QUANTUM-THEORY.....	1
II.—THE RADIATION PROBLEM, ACCORDING TO THE CLASSICAL MECHANICS.....	6
III.—THE DEVELOPMENT OF THE QUANTUM-THEORY	19
IV.—THE SPECTRA OF THE ELEMENTS AND THE EMISSION OF RADIATION	32
V.—THE PHOTO-ELECTRIC EFFECT AND THE ABSORPTION OF RADIATION	45
VI.—THE SPECIFIC HEAT OF SOLIDS.....	51
VII.—THE DYNAMICS OF THE QUANTUM-THEORY.....	61
VIII.—THE PHYSICAL BASIS FOR THE QUANTUM-THEORY.....	78
INDEX.....	85

CHAPTER I.

ON THE NEED FOR A QUANTUM-THEORY.

Introductory.

1. The quantum-theory, which is now found to be applicable in many departments of physical science, had its origin in an attempt to account for the spectrum of black-body radiation. It is therefore appropriate, as well as convenient, that the present report should approach the theory through the radiation problem. The arrangement adopted will be as follows : We shall first explain how the quantum-theory is demanded, and indeed made inevitable, by the known facts of black-body radiation (Chapters I. and II.) ; we shall next discuss the radiation problem with the help of the quantum-theory (Chapter III.), and shall then proceed to consider the bearing of the quantum-theory on certain other problems of physics, namely, the line spectra of the elements (Chapter IV., and again in Chapter VII.), the photo-electric effect (Chapter V.), and the specific heats of solids (Chapter VI.). Chapter VII. **will** report the progress made towards unravelling the general system of quantum dynamics, after which a final chapter (Chapter VIII.) will be devoted to discussing whether a physical basis can be found for the conceptions of the theory.

2. The quantum-theory, it will be understood from the outset, represents a complete departure from the old Newtonian system of mechanics. Until the end of the last century, the Newtonian mechanics had shown a capacity of explaining and interpreting practically all the phenomena to which it had been applied. It was natural that physical science should attempt to progress by explaining more and more phenomena in terms of the Newtonian mechanics. It was hoped that whatever phenomena still defied explanation would, with the acquisition of more intimate knowledge, be ultimately found to be simply further illustrations of the truth of the Newtonian system of laws.

Gradually certain phenomena have emerged from the general mass as resisting explanation in terms of these laws, and the conviction that something outside the Newtonian laws is needed for their explanation has now become firmly established. Of course, the mere discovery that a phenomenon is difficult to explain in the Newtonian way is no adequate reason for abandoning a system of laws which is known to hold throughout vast regions of natural phenomena ; what we have to discuss is whether there are not certain phenomena which are in flat contradiction to the Newtonian laws. From demonstrating that a matter is difficult to proving that it is impossible is a long step, but if this step can be taken with respect to the explanation of even one well-established phenomenon of Nature, then the logical necessity of rejecting the impossibility becomes unanswerable.

The phenomenon which provides the simplest crucial test as to the universal validity of the Newtonian mechanics is found to be the following : *When radiant*

2 *Radiation and the Quantum-Theory.*

energy is in temperature-equilibrium with matter, the total radiant energy per unit volume is finite, and not infinite. We shall see almost at once that this phenomenon is incompatible with Newtonian mechanics. Of course, it cannot be denied that the phenomenon itself is in some ways open to question. It may be argued that there are at least the possibilities that radiation never can be in temperature-equilibrium with matter, or that energy dissociated from matter is a figment of the imagination. These possibilities must, of course, be discussed. It may be argued that the mathematical proof is open to question: the proof was originally given by Poincaré, and the essential validity of his mathematical reasoning has never been seriously challenged, but this cannot carry absolute conviction. Like every other scientific judgment the matter has to be one of balancing probabilities. But a search for the considerations to be put in the other side of the balance reveals, to many minds at least, a total deficiency of real logical arguments. We, as physical machines, are built on a scale which is large compared with the scale of light-waves and electrons; from which it has resulted that our first physical experiments, as a race, have been concerned with matter also on a scale very large in comparison with its ultimate structure. The Newtonian laws have undoubtedly been found adequate to explain the whole series of what we may call large-scale phenomena, but no adequate reasons have, so far, been given for asserting that they must also be the laws which govern small-scale phenomena. The fact seems to be that the old laws are not, so to speak, fine-grained enough to supply the whole truth with regard to small-scale phenomena.

In view of the fact that our preconceived ideas must necessarily form the starting point in every train of thought, and that these preconceived ideas are very intimately bound up with the Newtonian mechanics, it seems advisable to begin the present report with an explanation of the reasons which are believed to compel the abandonment of this system. In the present chapter these reasons are discussed in a purely physical way, without mathematical analysis and therefore, of course, without rigorous proof. In the next chapter the mathematical analysis is given, but both in the present and the succeeding chapters an effort has been made to arrange the report so that the mathematical parts may be omitted, without losing the thread of the argument, by those readers whose interest centres mainly in physical ideas rather than in abstract reasoning.

The Crucial Phenomenon.

3. As has already been stated, the phenomenon which it is convenient to consider first, as providing a crucial test of the Newtonian mechanics, is the phenomenon that *the total radiant energy per unit volume in temperature-equilibrium with matter is finite, and not infinite.*

To understand the meaning of this phenomenon, and at the same time to make the question as definite and as simple as possible, let us fix our attention on an enclosure with perfectly reflecting walls in which there is a mass of iron at $0^{\circ}\text{C}.$, and let us suppose that there is a state of equilibrium inside this enclosure. The iron is continually radiating energy from its surface into the space inside the enclosure, and is also absorbing energy from this space. From the condition of equilibrium, the rates of exchange must just balance. If we assume, for additional simplicity, that the iron is coated with a perfectly absorbing paint, then in point

of fact each square centimetre of surface radiates 3×10^5 ergs of energy per second into the surrounding space, and also absorbs 3×10^5 ergs per second of radiation falling on to it from this space. The energy in those parts of the enclosure which are not occupied by matter is of density 4×10^{-5} ergs per cubic centimetre; the heat energy in the iron is of the order of 8×10^9 ergs per cubic centimetre, or 2×10^{14} times the energy density of the unoccupied space. The heat energy of the iron, as we know, resides in the oscillations of its atoms, each atom moving with an average velocity of about 30,000 cm. per second, and we have seen that after thermodynamical equilibrium has been attained, practically all the energy inside the enclosure will reside in these atomic oscillations.

4. A very little consideration will show that this state of things is different from what might be expected by analogy from other systems which are known to obey the ordinary dynamical laws. Consider, for instance, a tank of water in which is floated a system of corks (to represent atoms of matter) connected by light springs or elastics so that they can oscillate relatively to one another. Suppose that initially the surface of the water is at rest. Let the system of corks be set into violent oscillation and placed on the surface of the water. The motion of the corks will set up waves in the water, and these waves will spread all over the surface of the water, undergoing reflection when they meet the walls of the tank. We know that ultimately the corks will be reduced to rest; the energy of their motion will be transformed first into the energy of waves and ripples on the surface of the water, and then, owing to the viscosity of the water, into heat energy in the water. A final state in which the corks continue to oscillate with extreme vigour while the water has almost no energy is unthinkable; we expect a final state in which practically all the energy has found its way into the water.

5. Let us examine another analogy. Let the corks be replaced by spherical lead shot, again connected by light springs, and let the system be suspended in a closed chamber containing air. After the system of shot has been started in violent oscillation, let the chamber be closed up. The motion of the shot will set up waves in the air, and these will again be dissipated by viscosity. A final steady state in which the spheres continue to oscillate with high velocities for ever is again unthinkable. In point of fact, we know that the final state will be one in which the spheres are all at rest in their positions of equilibrium, or rather, to be quite precise, in which they oscillate with the infinitesimally small velocities of the Brownian movements appropriate to particles of their size; practically all the energy will have passed from the spheres into the surrounding air.

The Kinetic Theory of Gases enables us to trace out the transformation of the energy which originally resided in the oscillations of the spheres. In the final steady state we know that this energy will be the heat energy of the air. Let us simplify the discussion by assuming that the air was originally at, or close to, the absolute zero of temperature, and suppose that in the steady state the temperature of the air is T . If there are N molecules of air, their energy in the steady state will be $\frac{5}{2}NRT$, and if there are n spheres, the energy of their Brownian movements will be $\frac{3}{2}nRT$, where R is the gas constant. The total energy in the steady state will be $(\frac{5}{2}N + \frac{3}{2}n)RT$, and T will be determined from the condition that this quantity must be equal to the total energy of the original oscillations of the spheres. Since N , the number of molecules, will be enormously large compared with n , the number

perhaps in non-material ether and perhaps in nothing at all. Thus, it may be argued, the difference in the cases we have been discussing may perhaps not be one of obedience or disobedience to the classical mechanics, but of the existence or non-existence of a surrounding medium. Our arguments may not prove the breakdown of the classical mechanics, but merely the non-existence of the ether.

It is greatly to be wished that the question of the existence or non-existence of the ether could be settled by such simple considerations ; unfortunately it cannot. The theory of relativity in effect requires that it shall be impossible to decide as to whether an ether exists or not, either by these or by any other purely mechanical considerations ; the equations of radiation and absorption of energy are precisely the same whether the energy is radiated into, and absorbed from, an ether or empty space. The analysis we shall now give will show that the existence or non-existence of an ether is wholly irrelevant to the question, so that if our analogies break down, it is not on the question of the reality of the ether. Leaving analogies behind, we proceed to discuss the real physical problem at issue.

CHAPTER II.

THE RADIATION PROBLEM, ACCORDING TO THE CLASSICAL MECHANICS.

8. Any formula which is to represent the partition of radiant energy in a steady state of dynamical equilibrium with matter must be derived by expressing that the amount of energy radiated by the matter is equal to the amount absorbed. If $\varphi(\lambda, T)d\lambda$ is the law of partition of energy according to wave-length, there must be an equation of the form

$$\frac{\partial \varphi}{\partial t} = E - A, \quad (3)$$

where E stands for the rate of emission of radiation by the matter and A for the rate of absorption; and the steady state is determined by the condition $\frac{\partial \varphi}{\partial t} = 0$, or $E = A$.

In general, it may be expected that several agencies will be at work in the processes of emission and absorption. Planck, in the famous Paper* in which the conceptions of the Quantum-Theory were first introduced, supposed that the emission and absorption were accomplished by "resonators" of perfectly definite periods. These cannot, of course, account for the whole of the emission and absorption; let the parts due to them be denoted by E_R, A_R . An agency which must contribute something to the emission and absorption is to be found in the motion of free electrons in the matter; let us denote their contributions by E_E, A_E . A further agency is the photo-electric effect; when an electron is discharged there is an absorption of radiation; when one recombines there will be an emission of radiation. Let the contributions of the photo-electric effect be denoted by E_P, A_P . Treating all other agencies in the same way, we shall have an equation of the form

$$\frac{\partial \varphi}{\partial t} = (E_R - A_R) + (E_E - A_E) + (E_P - A_P) + \dots \quad (4)$$

The absorptions $A_R, A_E, A_P \dots$ may each be expected to contain φ as a factor; if we double the radiant energy of any wave-length we expect twice as much to be absorbed. Let us then put $A_R = B_R \varphi$, &c. In general, the emissions E_R, E_E, \dots will not depend on φ , but let us make the matter as general as possible by assuming that they each contain a term in φ . Let us then put $E_R = F_R + G_R \varphi$, &c., in which any or all of the G 's may vanish. We then have

$$\frac{\partial \varphi}{\partial t} = (F_R + G_R \varphi - B_R \varphi) + (F_E + G_E \varphi - B_E \varphi) + (F_P + G_P \varphi - B_P \varphi) + \dots$$

and the equation giving the steady state, obtained by equating the right-hand member of this equation to zero, is

$$\varphi = \frac{F_R + F_E + F_P + \dots}{(B_R - G_R) + (B_E - G_E) + (B_P - G_P) + \dots} \quad (5)$$

It is to be expected that the ratios of the different terms, both in the numerator and

* Annalen. d. Physik, 4, p. 553 (1901).

denominator, will vary from substance to substance. For instance, F_E and $B_E - G_E$ will be small for insulators or bad conductors in which there are few electrons, F_R and $B_R - G_R$ will be small for substances which possess few resonators of the frequency under consideration, and F_P and $B_P - G_P$ will be small for substances in which the photo-electric effect is slight at this frequency. On the other hand, observation shows that φ has precisely the same value for all substances. Now in order that φ may be the same for all substances, no matter what the relative values of F_R , F_E , F_P , &c., may be, it is necessary, as a matter of algebra, to have

$$\frac{F_R}{B_R - G_R} = \frac{F_E}{B_E - G_E} = \frac{F_P}{B_P - G_P} = \dots = \varphi, \quad \dots \dots \dots (6)$$

giving at once $E_R = A_R$, $E_E = A_E$ and $E_P = A_P$.

In other words, each agency in the mechanism of emission and absorption must, considered by itself, be capable of setting up the full black-body radiation, and must not set up any radiation different from this; if this were not so, the black-body radiation would vary from substance to substance.

Algebraically, it is of course conceivable that one agency might have so slight an influence that φ , as given by equation (5), might have a value indistinguishable from its true value, while the fraction corresponding to this agency in equation (6) might have a value widely different from φ . The numerator and denominator would simply have both to be very small. But physically this would be inconsistent with the second law of thermodynamics;* and, in fact, it would require that in the final steady state energy should continuously flow in a closed cycle through the different mechanisms in turn, a possibility which may be excluded from serious consideration.

We now proceed to consider the radiation from these different agencies in turn, beginning with that from "resonators."

Radiation from Resonators.

9. Let a resonator be considered as a dynamical system, and let its motion be assumed, for the present, to obey the classical laws. Let its frequency be $p/2\pi$, and let its kinetic and potential energies T and V be supposed given by

$$T = \frac{1}{2}\beta \dot{\varphi}^2, \quad V = \frac{1}{2}\alpha \varphi^2,$$

where φ is the co-ordinate expressing the state of the resonator and α and β are constants such that $p^2 = \alpha/\beta$.

The equation of motion, expressing the change in φ , is

$$\beta \ddot{\varphi} + \alpha \varphi = \Phi, \quad \dots \dots \dots (7)$$

where Φ is the generalised force acting to increase φ . On multiplying by $\dot{\varphi}$, we obtain

$$\frac{d}{dt} (T + V) = \Phi \dot{\varphi},$$

so that the energy gained by the resonator in the time from 0 to t is

$$\int_0^t \Phi \dot{\varphi} dt \quad \dots \dots \dots (8)$$

* Cf. Poincaré, Journ. de Phys., 11, p. 34 (1912).

The solution of equation (7) can be written down in the usual way.* Suppose that at time $t=0$, the values of φ and $\dot{\varphi}$ are the same as if the resonator were performing an oscillation specified by $\dot{\varphi}=A \cos (pt-\varepsilon)$. The impulse $\Phi_v dt$, acting through the small interval dt at time t' , produces a superimposed oscillation such that the value of $\dot{\varphi}$ initially is $\frac{1}{\beta} \Phi_v dt$, and, therefore, such that the subsequent value of $\dot{\varphi}$ is $\frac{1}{\beta} \Phi_v \cos p(t-t')dt$. Hence the total value of $\dot{\varphi}$ after time t is

$$\dot{\varphi} = \frac{1}{\beta} \int_{t'=0}^{t'=t} \Phi_v \cos p(t-t') dt + A \cos (pt-\varepsilon),$$

and the total absorption in time t , as given by expression (8), is

$$\int_0^t \Phi \dot{\varphi} dt = \frac{1}{\beta} \int_0^t \int_0^{t'} \Phi_v \Phi_{v'} \cos p(t'-t'') dt' dt'' + \int_0^t A \cos (pt-\varepsilon) \Phi dt.$$

On summing over a great number of oscillations, the second term on the right may be neglected, and the equation written in the form

$$\int_0^t \Phi \dot{\varphi} dt = \frac{1}{2\beta} \int_0^t \int_0^{t'} \Phi_v \Phi_{v'} \cos p(t'-t'') dt' dt'', \quad (9)$$

the divisor 2 appearing because the integration is over a square in the $t't''$ plane instead of over the half-square bounded by the line $t''=t'$.

The value of Φ from time 0 to t can be expressed as a Fourier series in the form

$$\Phi = \frac{1}{\pi} \int_0^\infty (F_p \cos pt + G_p \sin pt) dp,$$

where the coefficients F_p, G_p are given by

$$F_p = \int_0^t \Phi_v \cos pt' dt' \quad (10)$$

$$G_p = \int_0^t \Phi_v \sin pt' dt' \quad (11)$$

and in terms of these coefficients equation (9) may clearly be expressed in the form

$$\int_0^t \Phi \dot{\varphi} dt = \frac{1}{2\beta} (F_p^2 + G_p^2) \quad (12)$$

But from a theorem given by Lord Rayleigh,†

$$\int_0^t \Phi^2 dt = \frac{1}{\pi} \int_0^\infty (F_p^2 + G_p^2) dp,$$

so that the mean value of Φ^2 from 0 to t , say $\bar{\Phi}^2$, is given by

$$\bar{\Phi}^2 = \int_0^\infty f(p) dp,$$

* Lord Rayleigh, *Theory of Sound*, § 66.

† *Phil. Mag.*, [5], 27, p. 466.

where $f(p) = \frac{1}{\pi t} (F_p^2 + G_p^2)$, and the mean rate of absorption is, from equation (12),

$$\frac{1}{t} \int_0^t \Phi \dot{\varphi} dt = \frac{1}{2\beta t} (F_p^2 + G_p^2) = \frac{\pi}{2\beta} f(p).$$

If the force Φ arises from an electric intensity X , we may assume $\Phi = cX$, where c is a constant. Assume the density of radiant energy, resolved into its constituent frequencies, to be $\int_0^\infty R(p) dp$ per unit volume; then the mean value of X^2 will be $\frac{4\pi}{3} \int_0^\infty R(p) dp$, and c^2 times this will be $\overline{\Phi^2}$, which is equal to $\int_0^\infty f(p) dp$. Thus

$$f(p) = \frac{4\pi}{3} c^2 R(p),$$

and the mean rate of absorption of radiant energy by the resonator is $\frac{\pi}{2\beta} f(p)$, or $\frac{2\pi^2 c^2}{3\beta} R(p)$.

If the radiating mechanism is electrical, we may take the emission in time t to be given by either of the equivalent forms

$$\int_0^t C \ddot{\varphi}^2 dt = - \int_0^t C \dot{\varphi} \ddot{\varphi} dt,$$

where C is a constant. (The left-hand member will give the expression of Larmor, the right-hand that of Lorentz.) On substituting for $\ddot{\varphi}$ from equation (7), the emission in time t is

$$-\frac{C}{\beta} \int_0^t \dot{\varphi} (\dot{\Phi} - \alpha \dot{\varphi}) dt.$$

On integrating (10) and (11) by parts

$$F_p = -\frac{1}{p} \int_0^t \dot{\Phi}_p \cos pt' dt'; \quad G_p = \frac{1}{p} \int_0^t \dot{\Phi}_p \sin pt' dt',$$

so that

$$\int_0^t \dot{\varphi} \dot{\Phi} dt = \frac{p}{2\beta} (G_p F_p - F_p G_p) = 0,$$

and the emission in time t is

$$\frac{C}{\beta} \int_0^t \alpha \dot{\varphi}^2 dt.$$

Thus the average rate of emission is

$$\frac{C}{\beta} \overline{\alpha \dot{\varphi}^2} = \frac{C}{\beta} p^2 \overline{\dot{\beta}^2},$$

where a bar over any quantity denotes that its average value is to be taken over the interval of time from 0 to t .

On equating emission and absorption, the condition for a steady state is found to be

$$R(p) = \frac{3C}{2\pi^2 c^2} p^2 \overline{\beta \phi^2},$$

so that, in the steady state, the partition of radiant energy must be

$$R(p)dp = \frac{3C}{2\pi^2 c^2} \overline{\beta \phi^2} p^2 dp. \quad (13)$$

As soon as the nature of the resonator is definitely known, C and c will be known.

For a Hertzian oscillator* $C/c^2 = \frac{2}{3V^3}$, where V is the velocity of light, so that

$$R(p)dp = \frac{\overline{\beta \phi^2}}{\pi^2 V^3} p^2 dp. \quad (14)$$

If the resonator consists of a single electron capable of oscillating with frequency p , $C = \frac{2}{3} \frac{e^2}{V^3}$, $c = e$, so that $C/c^2 = \frac{2}{3V^3}$ as before, and formula (14) again gives the partition of energy.

Radiation from Free Electrons.

10. A free electron may to some extent be treated as a resonator of zero frequency in the sense that it is the limit of an oscillating electron when the forces acting on it are made to vanish. We can suppose the ϕ of the preceding analysis to be a co-ordinate x measured in any direction; the kinetic energy T of this motion is $\frac{1}{2} m \dot{x}^2 = \frac{1}{2} m u^2$, so that $\beta = m$. Again $C = \frac{2}{3} \frac{e^2}{V^3}$, $c = e$, so that formula (14) is true, but now only for the limit in which $p = 0$. The formula becomes

$$R(p)dp = \frac{m u^2}{\pi^2 V^3} p^2 dp \quad (15)$$

This gives the limiting form of $R(p)$ when $p = 0$. The general form can be found in the following way:—

A single ray of light propagated parallel to the axis of x will be specified by equations of the form

$$X=0, Y=A \cos \kappa(x+Vt), Z=0,$$

$$a=0, \beta=0, \gamma=-A \cos \kappa(x+Vt).$$

The motion of an electron moving in the field of force arising from this wave of light may be regarded as compounded of—†

(i.) A uniform velocity of translation of components u_0, v_0, w_0 —the undisturbed velocity of the electron.

* Planck gives a slightly different proof for the Hertzian oscillator; see *Acht Vorlesungen über Theoretische Physik*, Lecture V., or *Ann. d. Physik*, 4, p. 556 (1901).

† A more rigorous proof and discussion will be found in a Paper in *Phil. Mag.*, p. 14, Jan. (1914).

(ii.) Oscillations parallel to the axes of x and y , each of a harmonic nature and of frequency $\kappa w/2\pi$, where $w=u_0+V$, this latter being, of course, obtained by modifying the frequency of the incident light in accordance with the Doppler principle, the relativity modification being disregarded since the velocity of the electron will be small in comparison with that of light.

According to the classical dynamics the electron will absorb light of frequency $\kappa V/2\pi$. The emitted light will be of different frequencies for different directions of emission; the frequency corresponding to any direction will be obtained by modifying the frequency $\kappa w/2\pi$ of the oscillation in accordance with Doppler's principle.

Let the usual polar co-ordinates r, θ, ϕ be taken, the electron being the origin and the axis of x being $\theta=0$. In any direction θ, ϕ the component of velocity of the electron will be

$$u_0 \cos \theta + v_0 \sin \theta \cos \phi + w_0 \sin \theta \sin \phi,$$

so that the frequency of the radiation emitted in this direction will be $p/2\pi$, where p is given by

$$p = \kappa w V / (V - u_0 \cos \theta - v_0 \sin \theta \cos \phi - w_0 \sin \theta \sin \phi) \quad \dots \quad (16)$$

Let the distribution of intensity of radiation in different directions be supposed given by the formula $I(\theta, \phi) \sin \theta d\theta d\phi$; let the mean value of $u_0^2 + v_0^2 + w_0^2$ averaged over a great length of time be c^2 , and let the proportion of the whole time in which the velocity components lie within a small range du_0, dv_0, dw_0 , be

$$Af\left(\frac{u_0^2 + v_0^2 + w_0^2}{c^2}\right) du_0 dv_0 dw_0.$$

Then the average total radiation emitted by the electron per unit time will be

$$\iiint \iiint Af\left(\frac{u_0^2 + v_0^2 + w_0^2}{c^2}\right) I(\theta, \phi) \sin \theta d\theta d\phi du_0 dv_0 dw_0,$$

where the integration is over all values of u_0, v_0, w_0, θ and ϕ , and the frequency of any particular element is given by equation (16).

This radiation can be analysed into its different frequencies by changing the variables from u_0, v_0, w_0, θ and ϕ to u_0, w_0, θ, ϕ and p by the help of equation (16) and then integrating with respect to u_0, w_0, θ and ϕ . The final result is necessarily of the form*

$$\int \frac{1}{p_0} \Phi\left(\frac{p}{p_0}, c^2\right) dp, \quad \dots \quad (17)$$

where p_0 stands for $\kappa V, 2\pi$ times the frequency of the incident light, and Φ is a function of which the particular form does not matter for the present purpose.

Clearly if the electron is acted on by a number of waves traversing the ether simultaneously the resulting emission of radiation will be the sum of a number of integrals, each of the type of (17).

Now suppose that the electron is in a region of space in which the law of partition of radiant energy is $R(p_0)dp_0$, this energy being distributed at random as regards

* For details, see the Paper already referred to.

direction. Suppose that a unit amount of energy of frequency p_0 is, as the result of interaction with the free electron, replaced by an amount of energy ψ of the original frequency p_0 , and a spectrum $fF(p_0, p)dp$ of scattered energy. From formula (17), $F(p_0, p)$ must be of the form

$$F(p_0, p) = \frac{1}{p_0} \Phi\left(\frac{p}{p_0}, c^2\right),$$

and from the conservation of energy we must have

$$1 - \psi = \int_0^\infty F(p_0, p) dp = \int_0^\infty \Phi\left(\frac{p}{p_0}, c^2\right) \frac{dp}{p_0} \quad \dots \quad (18)$$

Clearly on integration this last is a function of c^2 only, so that ψ is independent of p_0 .

After unit time the law of partition of the whole amount of radiation will be

$$\psi \int R(p_0) dp_0 + \int dp \int_0^\infty R(p_0) F(p_0, p) dp,$$

or, arranged according to frequency p ,

$$\int \left[\psi R(p) + \int_0^\infty R(p_0) F(p_0, p) dp_0 \right] dp \quad \dots \quad (19)$$

The condition that the system shall have reached a final steady state is that the partition of radiant energy shall be unaltered by the interaction with the electron. The final partition of energy (19) must accordingly be identical with the initial partition of energy $fR(p)dp$, so that we must have

$$\psi R(p) + \int_0^\infty R(p_0) F(p_0, p) dp_0 = R(p)$$

or

$$R(p)(1 - \psi) = \int_0^\infty R(p_0) \Phi\left(\frac{p}{p_0}, c^2\right) \frac{dp_0}{p_0}.$$

The solution of this integral equation will give the form assumed by $R(p)$ in the steady state. If we put $p_0 = \chi p$, the equation becomes

$$\int_{\chi=0}^{\chi=\infty} \frac{R(\chi p)}{R(p)} \Phi\left(\frac{1}{\chi}, c^2\right) \frac{d\chi}{\chi} = 1 - \psi,$$

so that $R(\chi p)/R(p)$ must be independent of p . It follows that $R(p)$ must be of the form $R(p) = Bp^n$, where B and n are constants, so that the partition of energy in the ether must be given by

$$R(p)dp = Bp^n dp.$$

The values of the constants B and n can at once be found by comparison with formula (15), which gives the limiting form of $R(p)$ when $p=0$. Clearly we must

have $n=2$ and $B = \frac{mu^2}{\pi^2 V^3}$, so that the general value of $R(p)$ must be given by

$$R(p)dp = \frac{mu^2}{\pi^2 V^3} p^2 dp \quad \dots \quad (20)$$

Thus the result obtained from the classical dynamics is that if $R(p)$ has this form there can be permanent equilibrium between the free electrons and radiation, but if $R(p)$ has any other form, there will be a continued adjustment and exchange of energy until $R(p)$ has assumed this form.

11. According to the kinetic theory of matter, the mean value of mu^2 for an electron, which has been denoted by $\overline{mu^2}$, ought to be equal to RT , where R is the gas constant and T the absolute temperature of the matter. Richardson and others have determined the value of mu^2 by direct experiment, and find that it is in point of fact exactly equal to RT . If we substitute this value for $\overline{mu^2}$, formula (20) becomes

$$R(p)dp = \frac{RT}{\pi^2 V^3} p^2 dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Again, the kinetic theory of matter tells us that the mean value of the kinetic energy of the resonator considered in § 9 ought, if the classical dynamics is true, to be given by

$$\overline{\beta \dot{\phi}^2} = RT,$$

so that formula (14), expressing the condition for equilibrium between the resonators and radiant energy, according to classical dynamical theory, becomes

$$R(p)dp = \frac{RT}{\pi^2 V^3} p^2 dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

which is identical with (21).

Radiation from Electron Orbits.

12. In § 10 we considered the transfer of energy between electrons and radiation on the supposition that the electrons were absolutely free, and acted on only by the forces arising from the radiation. A somewhat different problem arises in the more natural case in which the free electrons are threading their way through the interstices of matter, and are in consequence experiencing accelerations and emitting radiation at each encounter with the atoms of the matter. The problem was first considered by Lorentz,* who found a formula giving the partition of radiant energy in the steady state for waves of great wave-length. Later the question was again attacked by the present writer,† who confirmed Lorentz's result by a different method, and showed how it could be extended to waves of all wave-lengths. The analysis of these papers is too long to be reproduced here, even in abstract, but the final result obtained is that the partition of energy of all wave-lengths must, in the final state of equilibrium, be given by

$$R(p)dp = \frac{RT}{\pi^2 V^3} p^2 dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

which, again, is identical both with (21) and (22).

13. The above formula, giving the partition of radiant energy according to frequency, is easily transformed into one giving the partition according to wave-

* "On the Emission and Absorption by Metals of Rays of Heat of Great Wave-length," Koninklijke Akad. van Wetenschappen, Amsterdam, April 24 (1903).

† Phil. Mag., p. 773, June (1909), and p. 209, July (1909).

length. Let the energy within a range $d\lambda$ of wave-length be $\varphi(\lambda, T)d\lambda$; then, since $\lambda = \frac{2\pi V}{p}$, the above formula becomes

$$\varphi(\lambda, T)d\lambda = 8\pi RT\lambda^{-4}d\lambda \quad \dots \dots \dots (24)$$

On comparison with formula (1) it is seen that the final partition of radiant energy predicted by the classical dynamics is exactly analogous to the partition of the energy of sound waves which occurs in a steady state in a gas. The sole difference lies in a multiplying factor 2, which, as we shall at once see, is readily explained by the difference between sound-waves and light-waves.

14. The physical interpretation of these formulæ is easily found. Consider any finite volume, v , of any homogeneous and continuous medium. The medium enclosed within this volume will be capable of executing a certain number of free vibrations, and associated with each free vibration will be its frequency $p/2\pi$ and the corresponding wave-length λ . When the wave-length is sufficiently small, the number of free vibrations for which λ lies within even a small range of values will be very great. Let us, in general, suppose that the number lying within a range $d\lambda$ is $f(\lambda)d\lambda$. Then clearly, $f(\lambda)$ will be proportional to v , and hence, from a consideration of physical dimensions, since $f(\lambda)d\lambda$ is to be a pure number, it must be of the form

$$f(\lambda)d\lambda = Cv\lambda^{-4}d\lambda,$$

where C is a constant. In other words, the number of vibrations per unit volume of the medium of wave-length between λ and $\lambda + d\lambda$ is $C\lambda^{-4}d\lambda$. The determination of the constant C for any medium is not difficult.* It is found that for the vibrations of sound in a gas $C=4\pi$, for the light vibrations in free ether, if an ether exists, $C=8\pi$, and for the elastic solid vibrations $C=12\pi$. If we like to assume that an ether does not exist, we may fall back on the general principle to which appeal has already been made, namely, that all observable phenomena must be precisely the same as if an ether did exist, and we shall find that $C=8\pi$ for the radiant energy in empty space.

The reason why the three values of C (4π , 8π , and 12π) are in the ratio 1 : 2 : 3 is obvious. In a gas there is only the one set of normal vibrations; in the ether there are only transverse vibrations, but there are two independent transverse vibrations, corresponding to two planes of polarisation, for each normal vibration in the gas; and in the elastic solid there are both normal and transverse vibrations.

15. In the sound formula (1) given in § 5, namely,

$$4\pi RT\lambda^{-4}d\lambda,$$

we note that the number of vibrations within the range $d\lambda$ of wave-length is $4\pi\lambda^{-4}d\lambda$, and therefore the average energy of each vibration is RT . In the radiation formula

$$8\pi RT\lambda^{-4}d\lambda \quad \dots \dots \dots (25)$$

the number of vibrations is $8\pi\lambda^{-4}d\lambda$, so that the average energy of each vibration is again RT . Thus the classical mechanics requires that, in the steady state of equilibrium, the average energy of each vibration shall be RT , whether in the ether or in a gas. A physical discussion of this is given later.

* Phil. Mag., p. 91, July (1905); H. A. Lorentz, The Theory of Electrons, § 73; also a purely mathematical Paper by H. Weyl, Math. Annalen, 71, p. 441.

The Theorem of Equipartition of Energy.

16. It has now been seen how the general result can be obtained that in the steady state the average energy of each vibration is RT , whether the vibration is a sound vibration in a gas, or a light vibration set up by resonators, or by free electrons radiating energy as they experience accelerations in an electric field, or by free electrons colliding with matter. This result is only part of a much more general result which can be obtained from the well-known theorem of equipartition of energy, a brief account of the proof of which may now be given, omitting all complications which have no bearing on the problems we are now concerned with.

Consider any dynamical system which will be supposed to move in accordance with the Newtonian laws, and let its condition be determined by n Lagrangian co-ordinates and the n corresponding momenta. Let these $2n$ quantities be denoted by $\theta_1, \theta_2 \dots \theta_{2n}$.

Then the condition of the system at any instant may be represented graphically by a point in an imaginary space of $2n$ dimensions, this point having for its Cartesian co-ordinates $\theta_1, \theta_2 \dots \theta_{2n}$. As the system follows out its natural motion this point will trace out a curve in the $2n$ dimensional space. We may suppose that the whole space is filled with representative points tracing out their appropriate curves, and in this way we can imagine that we have a graphical representation which enables us to study simultaneously all motions possible for our dynamical system.

According to the well-known theorem of Liouville,* the density of any group of points in this space does not change as the points follow out the paths descriptive of the natural motion of the system, provided this motion is in accordance with the Newtonian mechanics. For instance, if the moving representative points are initially sprinkled with uniform density throughout the space, they will remain of uniform density for ever.

Suppose it is found that after the steady state has been reached—i.e., after the motion has gone on for so long that the influence of the initial conditions has been obliterated—the system invariably possesses some definite property P . This might be from one of two reasons: Either that the representative points tend in their motion to cluster in those regions of the generalised space in which the property P holds, or that the property P is common to the whole of the generalised space. Liouville's theorem shows that the first of these cannot be the true reason. The property P must be common, then, to the whole of the generalised space. Strictly speaking, no property of any physical interest can be found which is common to absolutely every point in the generalised space, but a number of properties can be found which are true with very insignificant exceptions, these exceptions being such as would escape notice in experimenting. Thus we may say that the properties to be looked for in the steady state of a system are those which are common to the whole of the generalised space, except for insignificant exceptions.

These somewhat abstract considerations may be illustrated by a concrete example of a non-dynamical kind.

Suppose that we have an army of a million men of average height 5 ft. 8 in. This army can be divided into two wings each of 500,000 men in approximately $10^{301.027}$ different ways. There will, perhaps, be a million ways of arranging the

* Boltzmann, *Vorlesungen über Gastheorie*, Vol. 2., pp. 66, 67; or Jeans, *Dynamical Theory of Gases* (3rd Edition), p 73.

men so that the average heights in the two wings may differ by as much as 2 in. ; there may be (say) 10^{100} ways in which the averages may differ by $\frac{1}{10^6}$ in. ; there will be, perhaps, 10^{1000} ways in which the average will differ $\frac{1}{10^{100}}$ th of an inch. But for the majority of arrangements the average heights will be almost exactly equal. With the figures we have taken the chance will be $10^{300,000}$ to 1 that the average height in the two wings will be the same to within $\frac{1}{10^{100}}$ th of an inch. It is not true to say that for all arrangements of the men the average heights in the two wings will be only imperceptibly different, and yet the odds are $10^{300,000}$ to 1 against this statement being untrue if the men are arranged at random.

So, in the generalised space under consideration, there will be no property absolutely true of the whole space, but a number of properties can be found which are true for all points in the space except for a number which constitute a perfectly insignificant fraction of the whole. In particular, the following is easily shown to be such a property.

Let two groups of terms be taken out of the expression for the energy, each consisting of a very large number (p, q) of squared terms. Then the property which is true within the limits explained is that the average value of each term in the group of p terms is equal to the average value of the q terms. If, as in the kinetic theory of gases, we take the average value of terms in either group to be $\frac{1}{2}RT$, then the value of the group of p terms will be $\frac{1}{2}pRT$, while that of the group of q terms will be $\frac{1}{2}qRT$. This is, in effect, the theorem of equipartition of energy.*

17. It will at once be seen that this result embraces all the results which have been obtained in this chapter. First let the system under consideration consist of ether together with matter of all kinds. The number of vibrations of the ether of wave-length between λ and $\lambda+d\lambda$ will be $8\pi v\lambda^{-4}d\lambda$, where v is the volume of ether considered ; and each vibration will give rise to two squared terms in the energy, one kinetic and one potential. The total number of squared terms representing the energy of all these vibrations will be $16\pi v\lambda^{-4}d\lambda$, and therefore their energy will be equal to this number multiplied by $\frac{1}{2}RT$, or to $8\pi RTv\lambda^{-4}d\lambda$. Dividing by v to reduce to energy per unit volume of ether, we obtain for the radiant energy of wave-length between λ and $\lambda+d\lambda$

$$8\pi RT\lambda^{-4}d\lambda,$$

which is identical with formula (24). Again, appealing to the principle that it cannot possibly make any difference to observed phenomena whether an ether exists or not, we find that the same law must give the partition of radiation in empty space in an etherless universe.

This formula was given by Lord Rayleigh and the present author in 1900 as being the formula which ought, on the Newtonian mechanics, to govern the partition of energy in the spectrum. It cannot be the true law, for the total energy obtained by integrating from $\lambda=0$ to $\lambda=\infty$ would be infinite for any finite value of T ; and if the total energy were finite the only possible value for T would be $T=0$.

This, in fact, is the prediction of the classical mechanics as to the final steady state. We are led to expect that all the energy of the matter will be dissipated away in the form of radiation into the adjoining space, just as in the analogies of

* For references to the various proofs which have been given see Jeans, *Dynamical Theory of Gases*, Ch. V., or *La Théorie du Rayonnement et les Quanta* (Gauthier-Villars, Paris, 1912), p. 71. Detailed proofs of the theorem will also be found in both these places.

§§ 4 and 5, where it was seen that a continuous medium had the capacity of extracting all the kinetic energy from a system immersed in it. It is to escape from this necessary consequence of the classical mechanics that the quantum-theory has been brought into being.

18. Before proceeding to discuss the development of the quantum-theory, we may draw attention to various attempts which were made, before the quantum-theory had become as well established as it now is, to escape from the necessity, imposed by the classical mechanics, that all available energy should be degraded into radiant energy of very short wave-length. The classical theory requires that this degradation should occur before a steady state of thermodynamical equilibrium is attained; the obvious loophole of escape was the supposition that the observed partition of energy represented states which were not true states of thermodynamical equilibrium at all. If it is supposed that the emitted radiation of the highest frequencies is in some way drained off or allowed to escape, so that the density of radiation always remains very small, then it is possible to obtain a definite law, which, in certain cases, may show some of the characteristics of the observed radiation law.

19. There is, however, no longer any reason why different assumed mechanisms of radiation should all lead to the same law of partition of radiant energy, and it is, in point of fact, found that they do not. The case which has received most attention is that of the radiation emitted by accelerated free electrons describing orbits under atomic forces. It is assumed at the outset that the electron describes its orbit in a space which is almost devoid of radiant energy, and this, as is now obvious, amounts to assuming that there is no thermodynamical equilibrium between the radiant energy and the matter. If the acceleration of the electron is produced by collisions with atoms, it is found that instead of obtaining the Rayleigh formula

[illegible]

we obtain* a formula of the type

$$8\pi RT\lambda^{-4}f\left(\frac{c}{\lambda}\right)d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

in which c is a quantity such that $\frac{c}{2\pi V}$ is comparable with the time of a collision between the electron and an atom. From what has already been said, it is clear that for very long waves $f\left(\frac{c}{\lambda}\right)$ must approximate to unity, while, if the collisions are all of equal duration, it can be shown that, when λ is very small, $f\left(\frac{c}{\lambda}\right)$ will tend to zero in the same way as $e^{-\frac{c}{\lambda}}$. Making the assumption that the motion of each electron is made up of a series of exactly similar collisions, separated by rectilinear free-paths, Sir J. J. Thomson† arrived at the formula

$$8\pi RT \lambda^{-4} e^{-\frac{c}{\lambda}} d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

which is, of course, a special case of (27).

* La Théorie du Rayonnement et les Quanta, p. 69; and J. H. Jeans, Phil. Mag., July and August (1909).

† *Phil. Mag.*, 14, p. 225 (1907).

The following considerations at once are suggested :—

I. To reconcile formula (27) with Wien's law (*cf.* §20 below), c must vary as $1/T$, so that the duration of a collision must be exactly proportional to $1/T$. This would be the case only if the atoms were centres of force repelling according to the law of the inverse cube,* but this is not a condition which can be easily reconciled with what is known about the structure of atoms and the motion of electrons.

II. It is, of course, possible to find the value of c which would be required to make formula (27) agree with Planck's formula. At ordinary temperatures the time of collision would have to be of the order of 10^{-14} second. Remembering that the velocity of the electron is of the order of 10^7 , it is clear that this time of collision is too large to reconcile with what is known about molecular or atomic dimensions.†

III. For formula (27) to agree with the observed black-body radiation, the value of c , and the time of a collision, would have to be exactly the same for all substances, a condition which cannot be reconciled with the known diversity of structure of different substances.

IV. The experiments of Richardson and Brown‡ and of others have shown that the velocities of the electrons in a solid are distributed according to Maxwell's law, so that the values of c must be different for different electrons and for different collisions.

On integrating for all possible velocities, it is found that the limiting form for $f\left(\frac{c}{\lambda}\right)$ when λ is very small, is not proportional to $e^{-\frac{c}{\lambda}}$ but to $e^{-\sqrt{\frac{c}{\lambda}}}$, and this cannot be reconciled with observation.§

* J. J. Thomson, *l.c. ante*.

† Phil. Mag., 20, p. 651 (1910).

‡ Phil. Mag., 16, p. 353 (1908).

§ Phil. Mag., 20, p. 650 (1910).

CHAPTER III.

THE DEVELOPMENT OF THE QUANTUM-THEORY.

20. The last chapter showed that, consistently with the assumption of thermodynamical equilibrium, the Newtonian system of equations could lead to only one formula for the partition of radiant energy, namely, $8\pi RT\lambda^{-4}d\lambda$, a formula which does not agree with experiment. In the present chapter it will be explained how Planck, starting from conceptions entirely different from those of the Newtonian mechanics, has arrived at a radiation formula which is in perfect agreement with observation, and how Poincaré has shown that the observed radiation formula can be derived from only one set of physical assumptions, namely, those of the quantum-theory.

The radiation which is in thermodynamical equilibrium with matter at temperature T is spoken of as "full radiation" or "black-body radiation" at temperature T . According to Stefan's law its total intensity is proportional to T^4 ; according to Wien's displacement law, its energy, distributed according to wave-length, is of the form

$$F(\lambda T)\lambda^{-5}d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

where F is a function, undetermined so far as Wien's law goes, of the product λT . From Wien's law, Stefan's law can be deduced at once on integrating from $\lambda=0$ to $\lambda=\infty$.

Both Stefan's law and Wien's law can be deduced from general thermodynamical considerations, but such considerations do not suffice to determine the actual form of the function F in Wien's law. Both of these laws can be tested experimentally, and they are found to be in agreement with observation. The form of the function F can be determined experimentally, and the form which has been found to agree most closely with experiment is that suggested by Planck in 1901 in a Paper* which has since provided the basis for the quantum-theory. Planck's form, derived from considerations similar to those on which the quantum-theory now rests, is

$$\lambda^{-5}F(\lambda T) = \frac{8\pi h\nu}{e^{h\nu/RT} - 1},$$

where ν is the frequency corresponding to wave-length λ , and h is the constant, now known as Planck's constant, of which the value is approximately †

$$h = 6.55 \times 10^{-27} \text{ (erg} \times \text{sec.)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Substituting this form for $F(\lambda T)$ into expression (29), the partition of full black-body radiation at temperature T is found to be

$$8\pi RT\lambda^{-4}d\lambda \frac{x}{e^x - 1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where x stands for $h\nu/RT$. This formula[†] is found to agree with experiment to

* Annalen der Physik, 4, p. 553 (1901).

† Cf. below, § 62.

within the errors of observation. We shall now see how it can be derived by making use of a system of dynamics which differs widely from the classical system.

21. In the ordinary theory of gases, the "probability" that a system shall have its co-ordinates (p_1, p_2, \dots) and momenta (q_1, q_2, \dots) within a range $dp_1 dp_2 \dots dq_1 dq_2 \dots$ is found to be of the form

$$Ae^{-2kE} dp_1 dp_2 \dots dq_1 dq_2 \dots,$$

where E is the energy of the system in this configuration, A is a constant and k is given by $2kRT=1$. Hence, if ε is any amount of energy, the probabilities of the system having energies $0, \varepsilon, 2\varepsilon, \dots$, will stand in the ratios

$$1 : e^{-2k\varepsilon} : e^{-4k\varepsilon} : \dots \quad (32)$$

Strictly speaking, the probabilities we are discussing are not those of the system having energies $0, \varepsilon, 2\varepsilon, \dots$ but of its co-ordinates lying within equal infinitesimal ranges of values $dp_1 dp_2 \dots dq_1 dq_2 \dots$ surrounding these energies.

Consider a very great number, M , of vibrations, and suppose that of these N have zero energy. Then the number which may be expected to have energy ε will be $Ne^{-2k\varepsilon}$, the number which may be expected to have energy 2ε will be $Ne^{-4k\varepsilon}$, and so on. If we suppose, purely as a conjectural hypothesis at present, that all of the M vibrations have their energies equal to one or other of the values $0, \varepsilon, 2\varepsilon, \dots$ then we must have

$$M=N(1+e^{-2k\varepsilon}+e^{-4k\varepsilon}+e^{-6k\varepsilon}+\dots)=\frac{N}{1-e^{-2k\varepsilon}} \quad (33)$$

The total energy of all these vibrations must be

$$\varepsilon Ne^{-2k\varepsilon} + 2\varepsilon Ne^{-4k\varepsilon} + 3\varepsilon Ne^{-6k\varepsilon} + \dots,$$

of which the value, on summing and using relation (33), is found to be

$$\frac{M\varepsilon}{e^{2k\varepsilon}-1} \quad (34)$$

If the particular vibrations are those of wave-length between λ and $\lambda+d\lambda$ in a unit volume of ether, the value of M must be taken to be (*cf.* § 14) $8\pi\lambda^{-4}d\lambda$, and formula (34) assumes the form

$$8\pi\lambda^{-4}d\lambda \frac{\varepsilon}{e^{2k\varepsilon}-1} \quad (35)$$

We can pass to the problem contemplated in § 15, namely, that of determining the radiation-formula predicted by the classical mechanics, by passing to the limit $\varepsilon=0$; for the vibrations are supposed capable of having energies $0, \varepsilon, 2\varepsilon, 3\varepsilon, \dots, \infty$, which, when $\varepsilon=0$, means simply that the energy can have any value. Now, when ε is small, the limiting value of $\frac{\varepsilon}{e^{2k\varepsilon}-1}$ is $\frac{1}{2k}$ or RT , so that formula (35) reduces to

$$8\pi RT\lambda^{-4}d\lambda \quad (36)$$

This agrees with formula (25). as of course it should, and so does not agree with observation.

The general formula (35), can, however, be put in the form

$$8\pi RT\lambda^{-4}d\lambda \times \frac{\frac{\varepsilon}{RT}}{e^{\frac{\varepsilon}{RT}} - 1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

and this will agree with Planck's formula (31), and so also with observation, if we define ε by

[illegible]

where h is Planck's constant, and ν is the number of vibrations per second.

The assigning of a finite value of h is in opposition to the classical mechanics, since it does not permit the energy to vary continuously. If the energy changes at all when h has a finite value, it can do so only by taking jumps of finite amount.

The foregoing method of arriving at Planck's radiation formula was first given by the present writer.* A very similar method has recently been proposed by Darwin and Fowler.†

Such methods probably provide the shortest way of illustrating the connection between Planck's fundamental equation (38) and his radiation formula (4). There are obviously, however, grave objections to supposing that the energies of the vibrations in the ether must be multiples of ε . For this involves that these energies can only alter by sudden jumps, and the occurrence of these jumps would seem to be inconsistent with the supposition that the energy is spread throughout the whole of the ether.

22. The original method of Planck[‡] was based on somewhat different physical ideas. Suppose that the M vibrations considered in § 21 are the vibrations of M resonators, each of frequency ν . Their total energy will be given by expression (34), so that the average energy of each vibrator will be $\frac{\varepsilon}{e^{2h\nu} - 1}$, and the average kinetic energy will be one-half of this, or

[illegible]

where $x = \frac{\varepsilon}{RT}$. The conditions for equilibrium between resonators and ether have been considered in § 9; we note that the average kinetic energy of a resonator must now, from formula (39), be supposed to be $\frac{x}{e^x - 1}$ times what it was supposed to be in § 9, and the result is that the radiation formula is equal to that previously found multiplied by $\frac{x}{e^x - 1}$. In other words, the radiation formula now obtained is that of Planck.

This is the way in which Planck originally derived his formula, but this method also is open to serious objections. For, in considering the partition of energy between the various resonators, it is assumed that the energy can only vary by jumps of

* Phil. Mag., 20, p. 953 (1910).

† C. G. Darwin and R. H. Fowler, *Phil. Mag.*, 44, p. 450 (1922).

‡ *Annalen der Physik*, 4, p. 556 (1901).

amount ϵ , while, in considering the partition of energy between resonators and ether, it has to be assumed, as in § 9, that the energy of the resonators can vary continuously.

We may notice that the method assumes that the energy of the various vibrations in the ether can vary continuously, and, this being so, the condition for equilibrium between ether and, for instance, free electrons, may still be expected to be that obtained in § 10. In other words, we should expect that the resonators would, so to speak, strive to set up Planck's partition of radiant energy, while the free electrons and other mechanisms would strive to establish the equipartition formula (36) of the classical mechanics. The result would be a compromise between the two laws. Worse than this, it would be a compromise which would depend on the relative numbers of Planck resonators and of free electrons (*cf.* § 8), and as the ratio of these would vary from one substance to another, there would be no definite law of radiation—the same for all substances—such as is demanded by observation.

23. Still another method of obtaining Planck's radiation formula has been suggested by Einstein.* Again it is supposed that a great number of molecules (or atoms or resonators) are engaged in the emission and absorption of radiation, but in place of assuming that the energy of these molecules can be only multiples of a fixed quantum ϵ , it is assumed that the molecules can exist only in certain definite states, which we shall number as 1, 2, 3, . . . , in which their energies have specified values $\epsilon_1, \epsilon_2, \epsilon_3, \dots$.

It is supposed that the number of molecules in states 1, 2, 3, . . . is N_1, N_2, N_3, \dots , and that there is thermodynamical equilibrium with a field of radiation in which the energy per unit volume is of the type required by Wien's displacement law (*cf.* equation (29)), namely

$$F(\lambda T) \lambda^{-5} d\lambda$$

As a result of the action of the radiation of wave-length intermediate between λ and $\lambda + d\lambda$, let it be supposed that a certain number of molecules pass from state m to state n , and a certain number from state n to state m . The number passing per unit time from state m to state n may reasonably be assumed to be proportional to N_m , the number of molecules in state m . We may also assume it to be proportional to the density of the radiation in question, and so may take it to be

$$\alpha N_m F(\lambda T) \lambda^{-5} d\lambda$$

By similar reasoning, the number which pass per unit time from state n to state m may be assumed to be

$$\beta N_n F(\lambda T) \lambda^{-5} d\lambda.$$

Einstein supposes that in addition to these transitions, which are produced by the incidence of radiation, there occur a further number of spontaneous transitions from the state of higher energy m to the state of lower energy n . Such transitions are of course strictly analogous to those which occur in the degradation of radioactive substances. Einstein supposes such spontaneous transitions from state m to state n to occur at a rate

$$\dot{\gamma} N_m$$

per unit time.

* *Phys. Zeitschrift*, 18, p. 122 (1917).

The condition for a steady state requires that the total number of molecules passing from state m to state n shall be precisely equal to that passing in the reverse direction. With the assumptions we have made the condition becomes

$$F(\lambda T) \lambda^{-5} d\lambda [\beta N_n - \alpha N_m] = \gamma N_m \dots \dots \dots (40)$$

and this may be regarded as an equation to determine $F(\lambda T)$, and hence also the law of distribution of radiant energy.

In precise analogy to our formula (32), Einstein assumes the numbers of molecules in states 1, 2, 3, , corresponding to energies $\epsilon_1, \epsilon_2, \epsilon_3, \dots$ to be

$$N_m = p_m e^{-\epsilon_m/RT}, \quad N_n = p_n e^{-\epsilon_n/RT}, \dots \text{etc.}, \dots \dots \dots (41)$$

The factors p_m, p_n, \dots may now be different, since it is no longer essential, as it was before, to assume that the ranges of the differentials must be of equal extent in each of the configurations m, n, \dots of the molecules. Substituting these values of N_m, N_n in equation (40), and dividing throughout by $e^{-\epsilon_m/RT}$, we obtain

$$F(\lambda T) \lambda^{-5} d\lambda [\beta p_n e^{(\epsilon_m - \epsilon_n)/RT} - \alpha p_m] = \gamma p_m \dots \dots \dots (42)$$

Obviously the right-hand member of this equation is independent of the temperature. When $T = \infty$, the factor $F(\lambda T)$ on the left may be supposed to become infinite, so that the factor in square brackets on the left must vanish when T is infinite, and this requires that $\beta p_n = \alpha p_m$. The equation accordingly assumes the form

$$F(\lambda T) \lambda^{-5} d\lambda = \frac{\gamma}{\alpha} \frac{1}{e^{(\epsilon_m - \epsilon_n)/RT} - 1} \dots \dots \dots (43)$$

On the left-hand T enters only through the product λT , so that the same must be true on the right-hand. Thus $\epsilon_m - \epsilon_n$ must be proportional to $1/\lambda$, or, what is the same thing, to the frequency ν . Let us take the relation to be

$$\epsilon_m - \epsilon_n = h\nu \dots \dots \dots (44)$$

where h is a constant (which will ultimately be identified with Planck's constant). The factor γ/α on the right-hand does not involve the temperature at all. Einstein determines its value from the assumption that at infinite temperature the radiation must have the value assigned to it by the classical mechanics, so that when $T = \infty$, the right-hand member of equation (43) must reduce to $8\pi RT \lambda^{-4} d\lambda$. Thus we readily find as the general form of the radiation law

$$F(\lambda T) \lambda^{-5} d\lambda = 8\pi RT \lambda^{-4} d\lambda \frac{e^{\frac{x}{e^x - 1}}}{e^x - 1} \dots \dots \dots (45)$$

where x is, as previously, equal to $h\nu/RT$; but h is now defined through equation (44).

We may notice here that Einstein's deduction of the law of radiation does not require that the energy of the molecules should occur in complete quanta. It requires that the molecules can exist only in certain definite states, and that when a molecule jumps from one state to another the accompanying loss or gain of energy

is always one complete quantum of the radiant energy emitted or absorbed. We may sum up Einstein's hypothesis as follows :—

The interchange of energy between matter and radiation is always by single complete quanta of radiant energy.

For comparison, we may remark that the hypothesis underlying our first deduction of the radiation law (§ 21) may be summed up in the words—

Radiant energy, regarded as vibrations of an ethereal medium, can exist only in complete quanta,

while Planck's original deduction of his law (§ 22) was based on the supposition that

The material energy of vibrating resonators can exist only in complete quanta.

24. The discussion of another mathematical problem finds a suitable place in the present chapter. The assumption that changes in the energy of resonators or vibrations follow the Newtonian laws leads, as we have seen, to the formula of Lord Rayleigh for the partition of radiant energy in temperature-equilibrium with matter, while the assumption that these changes occur by jumps of amount $\varepsilon = h\nu$ leads to Planck's law. The converse problem demands consideration, at least in the special case of Planck's law, which is known to agree with observation. The problem is the following : Given that the final partition of energy is that given by Planck's law, what laws of motion must be postulated for the system in order to obtain this law ?

This problem has been solved with great completeness by Poincaré.* In 1921 R. H. Fowler† pointed out a want of rigour on the purely mathematical side in Poincaré's proof, and strengthened the argument by supplying the missing steps. The result obtained by Poincaré and confirmed by Fowler is, in brief, that no system can possibly lead to Planck's law, except one in which the assumption of the quantum-theory is satisfied : "L'hypothèse des quanta est la seule qui conduise à la loi de Planck."‡ Unfortunately, Poincaré's Paper is of such an abstruse mathematical nature that it is impossible to do any sort of justice to it in an abstract ; the reader who wishes to understand it must turn to the original Paper.

The following investigation of the same question,§ although less complete than that of Poincaré, is based on similar ideas, and leads to the same conclusions.

Consider the system discussed in § 16, and let the values of the quantities $\theta_1, \theta_2, \dots$ be represented in a generalised space, just as before ; again, let all possible states and changes of the system be represented by swarms of moving points.

In the former investigation, the systems represented by the moving points were supposed to obey the laws of the classical mechanics. It followed from the theorem of Liouville that there was no concentration of the swarms of points ; they moved indifferently through the whole space, and, as equipartition was a property of the whole space, it followed that equipartition ultimately ensued for all the systems.

We are now searching for a final result different from equipartition, so that we must no longer suppose that the swarms of points move without any concentration taking place, as they would do if the Newtonian laws held. Whatever laws or

* Journal de Phys., January (1912).

† Proc. Roy. Soc., 99 A, p. 462 (1921).

‡ Poincaré ; *l.c.*, p. 37.

§ Phil. Mag., 40, p. 943 (1910).

systems of equations govern the motion of the system, we must suppose some definite law of causation to hold—this is a necessary condition for the problem being capable of discussion at all. A system of particles endowed with free-will would not be a fit subject for mathematical treatment. It must be supposed, then, that the moving points in the generalised space follow definite tracks through the space, and, this being so, it is possible so to arrange the initial swarm of particles that the density at any point of the space remains always the same,* and does not vary with the progress of the motion. It is now only necessary to consider this permanent arrangement of density.

If the density of these swarms of points differed only by finite amounts, we should still be led to equipartition of energy and the radiation formula (25) of the last chapter. For, always excepting infinitesimal fractions, equipartition holds for all of the generalised space, and so, if the density were finite everywhere, would hold for all the representative points. The only way of avoiding the equipartition formula is to suppose that the density of the swarms of points must be zero throughout the whole, except for infinitesimally small regions, of the generalised space. There must be isolated small regions R_1, R_2, \dots in the generalised space occupied by dense swarms of points; in all other regions the density of points must be zero or infinitesimal. And, in order to satisfy the hydrodynamical equation of continuity in the generalised space, the motion of the points must consist of sudden jumps from one of the regions R_1, R_2, \dots to another. It appears in this way that, as soon as we seek to avoid the equipartition formula (25), we are compelled to assume motion involving discontinuities of some kind.

This result is so entirely identical with that obtained by Poincaré that we may, without break of thought, pass to his discussion of it.†

“All the states of the system which are represented in any one of these regions [called R_1, R_2 above] are indistinguishable from one another; they constitute one single definite state, so that we are led to the following proposition, one which is more definite than that of M. Planck, but not, I think, contrary to his ideas:—

“*A physical system is only susceptible of a finite number of distinct states; it jumps from one of these states to another without passing through a continuous series of intermediate states.*

“Suppose, to take a simplified illustration, that the state of the system depended only on three co-ordinates, x, y, z , so that we could represent it by a point in ordinary space. The swarm of points representing the different possible states will no longer fill the whole of this space or a region of this space in the ordinary sense; there will be a great number of isolated points scattered through space. These points, it is true, are very close together, which gives us the illusion of continuity.*

* The argument in more detail will be found in Poincaré's Paper or the Paper already referred to, *Phil. Mag.*, 40, p. 943 (1910).

† *Dernières Pensées*, p. 185. (I have translated freely.)

* That is to say, when we look at them on the scale of the ordinary mass-phenomena of nature. But in considering phenomena concerned with atoms, electrons, &c., we assume, so to speak, a mental microscope, and on looking at the points through a mental microscope of this power, they are seen to be widely separated. How wide, judged on this scale, is the gap that separates one point from its nearest neighbour will be clear from the calculations given in § 29 of the present report.—J. H. J.

"All these states must be regarded as equally probable. Indeed, if we admit determinism, to each of these states must necessarily succeed another state, which is just equally probable, since it is certain that the first is followed by the second. Thus one can see step by step that if we start from any initial state, all the states to which we shall arrive in time must be equally probable; all others must not be regarded as possible states at all.

"But our representative isolated points must not be scattered in space in any fashion we please; they must be distributed in such a way that in observing them with our coarse-grained appliances we have been led to believe in the ordinary dynamical laws, in particular in the laws of Hamilton. A comparison which approaches nearer to the reality than might be thought will make this clearer. The appearance of a liquid suggests at first that its structure is continuous; observation shows that the liquid is incompressible, so that the volume of any portion of its matter remains constant. Certain reasons then lead us to suppose that this liquid is composed of molecules, very small and very numerous, but discrete. We cannot now suppose the distribution of these molecules arranged in any way we fancy; the incompressibility of the liquid compels us to suppose that two equal small volumes contain the same number of molecules. In his distribution of possible states, M. Planck finds himself limited in a similar way.

"One might, it is true, imagine hybrid hypotheses. Let us return to the system which we supposed specified by three co-ordinates, so that its state could be represented by a point in space. The regions occupied by the representative points might be neither a continuous region in space nor a collection of isolated spots: it might be composed of a great number of small distinct surfaces, or of small distinct curves. It might be, for instance, that one of the material points of a system might describe only certain trajectories, and might describe them in a continuous manner except when it jumps from one trajectory to another under the influence of its neighbours; this might be the case with the resonators considered above. Or, again, the state of the ponderable matter might vary in a discontinuous way, with only a finite number of possible states, while the state of the ether varied in a continuous manner."

25. All this has followed merely from the hypothesis, or rather the fact, that the energy in the spectrum does not obey the equipartition formula of the classical mechanics. Let us next consider what particular form of discontinuities must be postulated in order to arrive at Planck's law.

Let the total energy E of the system be supposed made up of separate parts E_1, E_2, \dots , this division being made in such a way that E_1 depends only on one certain group of the co-ordinates $\theta_1, \theta_2, \dots$, E_2 depends only on a certain other group of co-ordinates and so on, no one co-ordinate entering into more than one group.

Let $W_{E_1} dE_1$ denote the proportion of the whole number of points for which E_1 has a value between E_1 and $E_1 + dE_1$; let $W_{E_2} dE_2$ denote the proportion for which E_2 has a value between E_2 and $E_2 + dE_2$, and so on. Then* the proportion for

* For details, see the Paper already referred to, *Phil. Mag.*, December (1910)

which E_1, E_2, \dots all lie within these specified ranges may be denoted by $W dE_1 dE_2 \dots$ and will be given by

$$W dE_1 dE_2 \dots = (W_{E_1} dE_1) (W_{E_2} dE_2) (\dots) \dots$$

in which W_{E_1} will be a function of E_1 only, W_{E_2} of E_2 only, and so on.

The most likely values for $E_1, E_2 \dots$ to have will, of course, be those which make W a maximum, or $\delta W = 0$. We have

$$\frac{\delta W}{W} = \frac{1}{W_{E_1}} \frac{\partial W}{\partial E_1} \delta E_1 + \frac{1}{W_{E_2}} \frac{\partial W}{\partial E_2} \delta E_2 + \dots \quad (46)$$

The total energy E of the system is supposed given; its value is

$$E = E_1 + E_2 + \dots,$$

so that

$$\delta E = \delta E_1 + \delta E_2 + \dots = 0 \quad (47)$$

and the condition that δW , as given by equation (46), shall vanish when $\delta E_1, \delta E_2, \dots$ are subject to the limitations expressed by equation (47) is

$$\frac{1}{W_{E_1}} \frac{\partial W}{\partial E_1} = \frac{1}{W_{E_2}} \frac{\partial W}{\partial E_2} = \dots \quad (48)$$

If one part of the system, say that of energy E_s , is supposed to be a gas thermometer, the value of the corresponding differential $\frac{1}{W_{E_s}} \frac{\partial W}{\partial E_s}$ can be readily calculated and is found to be $\frac{1}{RT}$. Thus the most likely set of values for E_1, E_2, \dots are those given by

$$R \frac{\partial}{\partial E_1} (\log W_{E_1}) = R \frac{\partial}{\partial E_2} (\log W_{E_2}) = \dots = \frac{1}{T}, \quad (49)$$

or

$$\frac{\partial S}{\partial E_1} = \frac{\partial S}{\partial E_2} = \dots = \frac{1}{T}, \quad (50)$$

where $S = R \log W$. It is now possible to identify S with the entropy;* the most likely values for E_1, E_2, \dots are simply those which make the entropy a maximum. It is easily shown that, for any system consisting of an enormously great number of parts, the regions in the representative space for which W is actually a maximum are enormously greater than all the others together. Thus, $\delta W = 0$ or $\delta S = 0$ expresses a true steady state. Since $S = R \log W$, it is the state simply in which the entropy is a maximum. The equations which express this are equations (50), which are now seen to be merely the expression of the second law of thermodynamics.

26. To examine what conditions will lead to Planck's law for the steady state, we have merely to identify the condition expressed by equation (49) or (50) with that expressed in Planck's formula.

Unfortunately the identification proceeds differently according to different physical interpretations of the meaning of radiation. If we regard radiation as the vibrations of an ethereal medium, then Planck's formula asserts that the

* Boltzmann, Vorlesungen über Gastheorie, I., § 6.

energy E_1 of M vibrations of frequency ν vibrations per second is given (cf. equation (34)) by

$$E_1 = \frac{M\varepsilon}{e^{\varepsilon/RT} - 1},$$

where $\varepsilon = h\nu$; whence, on solving for T ,

$$\frac{1}{T} = \frac{R}{\varepsilon} \log \left\{ 1 + \frac{M\varepsilon}{E_1} \right\},$$

and, from relations (49)

$$\frac{1}{T} = R \frac{\partial}{\partial E_1} (\log W_{F_1}).$$

Thus

$$\frac{\partial}{\partial E_1} (\log W_{F_1}) = \frac{1}{\varepsilon} \log \left(1 + \frac{M\varepsilon}{E_1} \right),$$

giving on integration

$$\log W_{F_1} = \left(M + \frac{E_1}{\varepsilon} \right) \log \left(M + \frac{E_1}{\varepsilon} \right) - \frac{E_1}{\varepsilon} \log \frac{E_1}{\varepsilon} + \text{cons.}$$

Write P for E_1/ε and use Stirling's approximation for factorials, and we obtain

$$W_E = C \frac{(M+P)!}{P!},$$

where C is a constant. But $\frac{(M+P)!}{P!}$ is the number of ways in which P articles can be put into M pigeon-holes, or, for our present purpose, is the number of ways in which P units of energy can be distributed between M vibrations capable of holding energy. Thus Planck's formula is obtained by supposing that the total energy E_1 is divided into P units (each of amount ε or $h\nu$, since $P = \frac{E_1}{\varepsilon}$) and that these are distributed among the M vibrations. Moreover, it is readily seen that this way of arriving at Planck's formula must be unique.

27. This result is the same as is arrived at in Poincaré's Paper, referred to above,* but Poincaré's method is one which makes it possible to proceed one stage further. Planck's law, if absolutely true, must, as has been seen, require the discontinuities of the theory of quanta. But, as Poincaré remarks,† a law found experimentally is never more than an approximation. Could we then imagine laws such that their differences from Planck's law would be within the errors of observation, but which would at the same time lead to a continuous system of dynamical laws ?

This question has already been answered in § 23, and in Poincaré's Paper a second decided negative is again given. It is shown that no small, or even finite, departures from Planck's law will dispose of the necessity for discontinuity. Poincaré

* Journ. de Physique, January (1912).

† *Loc. cit.*, p. 27.

shows definitely and conclusively that the mere fact that the total radiation at a finite temperature is finite (the crucial fact referred to in § 2) requires that the ultimate motion should be in some way discontinuous—*

“Quelle que soit la loi du rayonnement, si l'on suppose que le rayonnement total est fini, on serait conduit à une fonction présentant des discontinuités analogues à celles que donne l'hypothèse des quanta.”

It seems then to be abundantly proved that the transfer of energy must in some way take place by jumps or jerks of amount $\varepsilon = h\nu$, but mathematical analysis gives no indication as to the physical nature of these processes. The physical problem as to when, where and how the jumps occur can be solved with much less certainty than the mathematical problem, of which the solution has predicted the occurrence of the energy jumps with a high degree of certainty. The consideration of the physical problem is deferred to the last chapter; we now proceed to consider some purely numerical consequences of the mathematical solution which has been obtained.

28. The formula given by the Newtonian mechanics for the partition of black-body radiation was

$$8\pi RT\lambda^{-4}d\lambda, \quad (51)$$

while the formula given by the quantum-theory is the same formula multiplied by

$$\frac{x}{e^x - 1} = \frac{1}{1 + \frac{1}{2}x + \frac{1}{6}x^2 + \frac{1}{24}x^3 + \dots}$$

in which $x = \frac{\varepsilon}{RT} = \frac{h\nu}{RT}$. From the above expansion it is clear that the energy given by Planck's formula is always less than that given by formula (51), and the divergence between the two formulæ increases as x increases—i.e., as we pass to higher frequencies or lower temperatures. The following table gives values of $x/(e^x - 1)$ for different values of x :—

x	$x/(e^x - 1)$	x	$x/(e^x - 1)$
0.0	1.000	2.0	0.313
0.2	0.903	2.4	0.239
0.4	0.813	2.8	0.181
0.6	0.730	3.2	0.136
0.8	0.653	3.6	0.101
1.0	0.582	4.0	0.0764
1.2	0.517	4.5	0.0505
1.4	0.458	5.0	0.0339
1.6	0.405	6.0	0.0149
1.8	0.357	7.0	0.0064

A graphical representation of Planck's formula and of formula (51), both arranged according to frequency, is given in Fig. 1, the thin line representing formula (51) and the thick line the formula of Planck. The characteristic difference between the two formulæ is, of course, that formula (51) increases indefinitely as the frequency

* *L.c.*, p. 29.

increases, whereas Planck's formula attains a maximum, and then very rapidly falls off again to zero.

29. It is found that Planck's formula represents the experimentally observed distribution of energy if

$$h = 6.55 \times 10^{-27} \text{ erg} \times \text{second}.$$

The value of the quantum of energy for any wave-length can be found at once. For instance, for the D-lines, $\nu = 5 \times 10^{14}$, so that

$$\varepsilon = h\nu = 3.28 \times 10^{-12} \text{ erg}.$$

This may be compared with the energies met with in the theory of gases. At 0°C ., $RT = 3.75 \times 10^{-14}$ erg, so that the energy of an atom of mercury vapour at

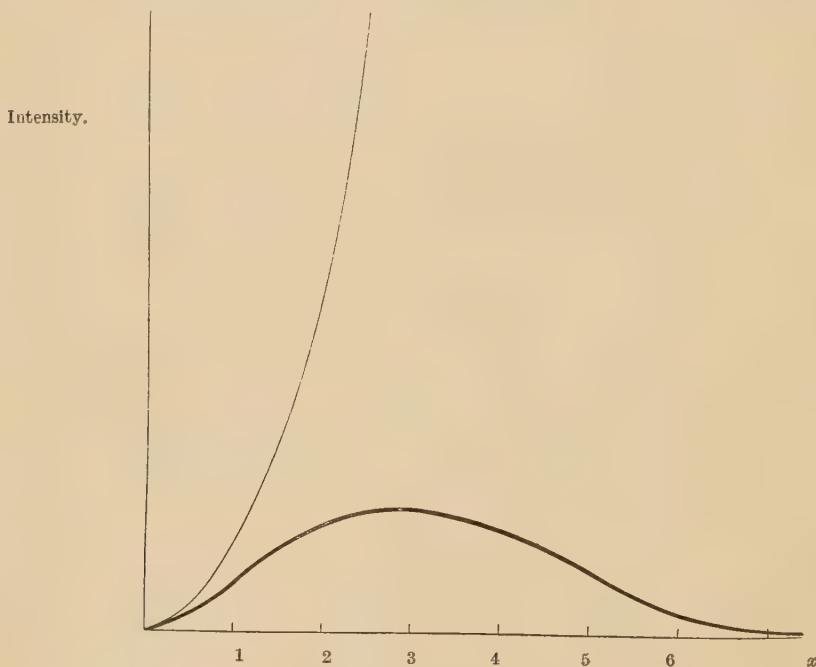


FIG. 1.

0°C . is 5.6×10^{-14} erg, and the quantum of yellow light is about that of *sixty* atoms of mercury, or other monatomic gas, at 0°C .

Again, the energy per atom of a hot solid is $3RT$, or $4 \times 10^{-16}T$. The radiation emitted by a solid at temperature T has its maximum ordinate λ_{max} , given by $\lambda_{\text{max}}.T = 0.29 \text{ cm.} \times \text{deg}$. The energy in a quantum of light of this wave-length is given by

$$\varepsilon = \frac{hV}{\lambda_{\text{max}}} = 7 \times 10^{-16}T,$$

so that the quantum of light of any colour contains as much energy as nearly two atoms of the solid at the temperature at which light of this colour is emitted.

Thus it appears that the quantum is by no means a small amount of energy when compared with atomic energies.

30. Of the M vibrations, whether of material resonators or of light, considered in § 21, N were supposed to possess no energy at all. Thus, out of the whole number, only a fraction $\frac{M-N}{M}$ possess any energy, and the value of this fraction, by equation (33), is $e^{-2h\epsilon}$ or $e^{-\epsilon/RT}$. If ϵ/RT is large, only a small fraction of the vibrations will possess any energy; the majority will be perfectly at rest.

For instance, at 0°C ., $RT=3.75 \times 10^{-14}$ erg, and the quantum for yellow light is 3.28×10^{-12} erg, so that $\epsilon/RT=\text{about } 87$, and $e^{-\epsilon/RT}=\text{about } 10^{-38}$. If we suppose that each molecule in a mass of matter at 0°C . has associated with it a vibration of frequency equal to that of the D lines, then only one out of every 10^{39} of these vibrations will have any energy. Only one molecule in 5×10^{10} tons will have any energy arising from this vibration to give out when in its steady state at 0°C .

Corresponding to the wave-length $\lambda_{\text{max.}}$, the value of the quantum is given by $\epsilon=4.965 RT$, so that even as regards light of wave-length $\lambda_{\text{max.}}$ at any temperature only one in $e^{4.965}$, or about 1 in 140, of the vibrations has any energy. Thus, in a red-hot mass of iron, less than 1 per cent. of the red vibrations have any energy: the remaining 99 per cent. are perfectly dead.

CHAPTER IV.

THE SPECTRA OF THE ELEMENTS AND THE EMISSION OF
RADIATION.

31. In the last two chapters it has been seen that mathematical analysis leads to the following quite definite results :

(i.) The final steady state of any system in which the laws of Newtonian dynamics are obeyed must be one in which the partition of radiant energy in temperature-equilibrium with matter is given by the formula

[illegible]

(ii.) To obtain a final steady state in which the partition of energy is given by Planck's law, and so agrees with observation, the motion of the system must be governed by the laws of the quantum-theory.

The laws of the quantum-theory have so far been obtained only in the mathematical form $\varepsilon = h\nu$, with the restriction that exchanges of energy equal to fractions of the quantum ε cannot occur. These laws do not amount to a complete system of dynamical laws; indeed, it could hardly be expected that the complete system of laws governing the ultimate processes of Nature could be obtained from a study of the one phenomenon of black-body radiation. The laws, in so far as we have been able to obtain them, give no information as to motion which is not of a vibratory nature; they give no information as to any vibrations except perfectly isochronous ones; they require that exchanges of energy should take place by multiples of the quantum ε , but give no information as to when or why these exchanges of energy may be expected to take place. Finally, they give no indication at all as to the seat of these quanta of energy, whether they are to be looked for in the radiation or in matter. The phenomenon of black-body radiation has yielded what information there is to be extracted from it; to complete our knowledge we must survey other phenomena of Nature. Incidentally, the discovery that other phenomena require laws similar to those of the quantum theory will help to confirm the results obtained from the study of black-body radiation.

So far as concerns the problem of black-body radiation, the formula derived from the Newtonian laws was found to give a good approximation to the truth so long as x is small, where

$$x = \frac{hv}{RT} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (53)$$

The numerator of the fraction x is $h\nu$, the quantum of energy ; the denominator is RT , which is the mean energy of a vibration of great wave-length, and would be the mean energy of all vibrations if the Newtonian laws held. When this quantity RT contains many quanta, x is small ; when it contains few quanta x is large. Thus the evidence of the phenomenon of black-body radiation suggests that the Newtonian laws begin to fail as soon as the average energy RT does not contain a great number of quanta. Perhaps, then, what is to be expected from the quantum-theory is not that it shall annihilate our belief in the Newtonian laws, but that it shall extend

and amplify these laws so as to cover large values of x in the radiation problem, and correspondingly in other problems.

Many similar cases of apparent failures of laws in physics at once suggest themselves. The laws of gases begin to fail when the gas does not contain a great number of molecules, the laws of electricity fail when the charges or currents do not contain a great number of electrons, and so on. The laws which appear to fail are applicable to large-scale phenomena only; they take no account of the atomic nature of some entity, and so fail when applied to small-scale phenomena. Boyle's law is, so to speak, too coarse-grained to apply to single molecules, Ohm's law is too coarse-grained to apply to a few electrons. In the same way the Newtonian laws are too coarse-grained to apply to one or a few quanta.

We have, however, seen that the Newtonian laws appear to apply, at any rate as an approximation, to the radiation problem when x is small—i.e., when T is very large or when ν is very small. When T is very large, energy is very abundant; there are a great many quanta involved, and the atomicity of the quanta is of no account. When ν is very small, the quanta ($h\nu$) are very small, and again the atomicity is of no account.

The atomicity involved is not necessarily an atomicity of energy. RT is average energy, $1/\nu$ is the time of a vibration, so that RT/ν is a physical quantity of dimensions (energy) \times (time). A quantity of these physical dimensions is spoken of as action. Thus, the Newtonian laws hold when the action RT/ν is great compared with the action h , of which the amount is known experimentally to be $h = 6.55 \times 10^{-27}$ erg \times second. An alternative way of looking at the matter would be to suppose that "action" is atomic, that there is a universal atom of action of amount h , that the Newtonian laws take no account of this atomicity of action, and so are only valid approximations when the amount of action involved is a very great multiple of h . This way of regarding the situation is not limited to problems dealing with isochronous vibrations.

In searching for other phenomena in which the Newtonian laws break down it is natural to examine closely those in which the temperature is very low, or the frequency of a vibration very high, or the "action" of a process very small. In point of fact, each of these alternatives is found to lead to one phenomenon of importance in connection with the quantum-theory, these being respectively the phenomena of specific heats at low temperatures, of the line spectra of the elements, and of the photo-electric effect. Purely for convenience of arrangement we may take the line-spectra first.

The Problem of the Line Spectra of the Elements.

32. So long as physicists thought in terms of the Newtonian mechanics almost every characteristic of the line-spectrum was a source of difficulty. The evidence both of emission and absorption suggested that the spectrum gave indication either of oscillations about a state of steady motion or of vibrations about a state of rest of the dynamical system forming the atom. The discovery of the Zeeman effect and the explanation of it given by Lorentz in terms of the electron theory seemed to confirm these conjectures, and supplied the further information that the moving charges which were the origin of the emitted light were the electrons.

The first serious difficulty in this view was one which presented itself to Maxwell

and Lord Kelvin. Each spectral line represented a separate vibration of the atom, and each vibration ought, according to the theorem of equipartition of energy, to have energy equal to RT . Thus a gas with n lines in its spectrum ought to have energy nRT per atom from its spectral vibrations alone. But the total energy of mercury is only $\frac{3}{2}RT$ per atom, which is fully accounted for by the kinetic energy of motion of the atoms; the total energy of hydrogen is only $\frac{5}{2}RT$ per molecule, and so on.

33. The difficulty of the problem has been in no sense lessened by the advent of more precise knowledge of the constitution of the atom. Following on the researches of Rutherford and his pupils, it is now generally accepted that the atom consists of a central nucleus of positive electricity around which are a number of negative electrons. When the atom is in its neutral (i.e., uncharged) state, the number of these electrons is such that their total charge is exactly equal and opposite to the charge on the nucleus. The number of electrons is also equal to the "atomic number" of the element.

Various experiments on the deflections of α and β particles have shown that the law of force of the central nucleus is that of the inverse square of the distance, at any rate, down to distances of the order of 10^{-12} cm. Now many lines of investigation show that the distance from the nucleus to the outer electrons of an atom is very much greater than this; this distance is known to be of the order of 10^{-8} cm. Thus the outer electrons are in a field of force in which the law of force is that of the inverse square, and it is well known that there can be no stable statical equilibrium in such a field. It is accordingly generally supposed that the electrons must be in some kind of orbital motion about the nucleus.

On this view, the uncharged hydrogen atom consists of a central nucleus of charge $+e$ about which a negative electron of charge $-e$ revolves in orbital motion; the uncharged helium atom consists of a central nucleus of charge $+2e$ with two negative electrons in orbital motion about it, and so on. It is possible for a helium atom to lose one of its attendant electrons; it then becomes a positively charged helium atom, and consists of a nucleus of charge $+2e$ with only one electron of charge $-e$ revolving about it.

34. Consider now the simplest atomic system, the normal hydrogen atom. Suppose that its two constituents, the nucleus and the electron, acted on one another according to the ordinary electrostatic law by which the force varies as the inverse square of the distance, and that they moved according to the classical Newtonian law by which the acceleration is proportional, in magnitude and direction, to the force. Then the positive nucleus, being approximately 1,845 times as massive as the electron, would remain practically at rest while the electron would describe an elliptical orbit about it. The radiation which, according to classical electrodynamics, would be emitted by an electron describing such an orbit admits, of course, of exact calculation, but for our present purpose it is sufficient to notice one general characteristic of the emitted radiation. As radiation is emitted, the energy of the atom diminishes, so that the orbit continually shrinks. Hence in a miscellaneous collection of hydrogen atoms there would be orbits of all possible sizes, and therefore of all possible periods. Hence the emitted radiation would necessarily be of all possible frequencies—in other words, the spectrum would be continuous. Inasmuch as the spectrum of the hydrogen atom consists of sharply defined lines, it is at once

clear that the motion of the two constituents of the hydrogen atom and their emission of radiation cannot be governed by the ordinary electrodynamic laws.

So far as our argument has at present proceeded, it is possible either that the electrostatic law of force or the classical electrodynamical laws may be at fault. It is, however, readily seen that the line-spectrum cannot be obtained by merely altering the electrostatic law of force while retaining the rest of the classical dynamics. To get a line-spectrum the law of force would have to be such that the orbits were isochronous—orbits of all sizes would have to be described with precisely equal periods. Now it is readily shown that the only law of force which leads to this isochronous property is that in which the force varies directly as the distance, and this law of force may at once be dismissed as being irreconcilable with the results of experiments on the scattering of α and β -rays. We conclude that the observed line-spectrum of hydrogen can only be explained by some alteration in the classical laws of dynamics. Moreover, the new system of dynamical laws must be in some way discontinuous in their nature, for it is readily shown that a continuous system of laws would lead to a continuous spectrum.

Similar conclusions were reached when we studied the spectrum of black-body radiation. In this instance it proved possible (§25), from a knowledge of the observed spectrum, to deduce a good deal as to the nature of the discontinuities in the dynamical laws. In the present instance, unfortunately, such a procedure is not possible; if we know the laws of motion we can determine the spectrum, but it does not prove to be possible, knowing the spectrum, to determine the laws of motion. This converse problem can be solved only by methods of trial and error.

In July, 1913,* Prof. Niels Bohr, of Copenhagen, propounded a solution which met with instant favour as giving an explanation of much that had defied explanation in terms of the classical mechanics, and which, after very slight modification, has now received practically universal acceptance on account of the complete agreement of its predictions with observation.

BOHR'S THEORY OF LINE-SPECTRA.

35. Bohr considers, in the first instance, the simplest case of an atom of only two constituents, an atom in which a single electron of mass m and charge $-e$ describes an orbit round a nucleus of charge E and of mass M so large that the nucleus may be supposed to remain at rest, at any rate for preliminary approximate calculations. He assumes the force between the electron and the nucleus to be that given by the ordinary electrostatic law of the inverse square, and in the first instance considers only circular orbits.

He takes ω to be the frequency of revolution of the electron in its orbit, so that $2\pi\omega$ is the angular velocity with which this orbit is described. Then, according to the Newtonian mechanics, the condition that a circular orbit of radius a may be possible is

$$\frac{eE}{a^2} = (2\pi\omega)^2 m \bar{a}. \quad \dots \dots \dots (54)$$

The kinetic energy of the electron is $\frac{1}{2}m(2\pi\omega a)^2$, or $\frac{1}{2}\frac{eE}{a}$. The work required

* Phil. Mag., 26, pp. 1 and 476 (1913), and later Papers in the Phil. Mag.

to move the electron from its orbit to a position of rest at infinity is $\frac{eE}{a} - \frac{1}{2}m(2\pi\omega a)^2$, or again $\frac{1}{2}\frac{eE}{a}$. If this quantity, the negative energy of the orbit, is denoted by W , it is readily found that

$$2a = \frac{eE}{W}; \quad \omega = \frac{\sqrt{2}}{\pi} \frac{W^{\frac{3}{2}}}{eE\sqrt{m}}. \quad \dots \dots \dots (55)$$

These equations have been obtained by the Newtonian mechanics. According to the Newtonian mechanics the loss of energy W ought to go on increasing as energy was dissipated by radiation, so that a would continually decrease and ω increase. The orbit would get smaller and more rapid until the electron fell into the nucleus, and, as this process was going on, the spectrum emitted by the system would naturally undergo continual change. These considerations illustrate in a forcible way the inability of the old mechanics to account for the line spectrum.

36. To avoid all these difficulties, Bohr introduces an assumption which is not inconsistent with the quantum-theory and is closely related to it. It has been noticed already that the quantum-theory is not in itself a complete system of dynamics, and so must not be expected to give a full account of phenomena by itself. The complete system of dynamics, of which it is a part, has not yet been found, and Bohr's assumption only amounts to adding tentatively one other brick to the foundation already laid by Planck's equation $\epsilon = h\nu$.

Bohr's assumption, introduced at present only with reference to the atom with one electron, is contained in the equation

$$W = \frac{1}{2}\tau h\omega \quad \dots \dots \dots (56)$$

in which h is Planck's constant and τ is an integer. Various physical interpretations can be given to this equation. Perhaps the simplest is the following: The angular momentum of the electron in its orbit is $2\pi m\omega a^2$ or $W/\pi\omega$. Bohr's assumption, expressed in equation (56), makes this equal to $\tau h/2\pi$, i.e., to an integral multiple of the universal constant $h/2\pi$, and so is equivalent to assuming that angular momentum is atomic, and that $h/2\pi$ is the unit. An alternative physical interpretation, less simple, but more in line with general quantum dynamics, arises from the circumstance that in a circular orbit the kinetic energy T is equal to W . Thus equation (56) expresses that the kinetic energy of the orbit must be an integral multiple of $\frac{1}{2}h\nu$, where ν is the frequency of the orbit. This may be compared with Planck's original assumption that the total energy, kinetic and potential, of a vibrator must be an integral multiple of $h\nu$, where ν is the frequency of the oscillator.

The effect of Bohr's assumption is, of course, to prevent the continuous variations of W , a and ω , which would be demanded by the Newtonian mechanics. The values of W , a and ω are found, from equations (55) and (56), to be

$$W = \frac{2\pi^2 m e^2 E^2}{\tau^2 h^2}, \quad 2a = \frac{\tau^2 h^2}{2\pi^2 m e E}, \quad \omega = \frac{4\pi^2 m e^2 E^2}{\tau^3 h^3}. \quad \dots \dots \dots (57)$$

Instead of τ varying continuously, as it would in the older mechanics, it is now restricted to integral values. How complete a difference there is between the two

systems will be realised on considering the variations of angular momentum demanded in the two cases. According to the classical mechanics, the electron experiences a retarding force, F , equal to $\frac{2}{3}\frac{e^2}{\sqrt{3}}(2\pi a\dot{\omega})$ from its interaction with the ether, and the rate of loss of its angular momentum $\tau h/2\pi$ is given by

$$\frac{h}{2\pi} \frac{d\tau}{dt} = -F,$$

while, according to the new hypotheses of Bohr, $d\tau/dt$ has no meaning at all!

The effect of restricting τ to integral values is that W , ω and a are limited to certain definite values. Thus a cannot gradually shrink, but the electron is limited to a circular orbit of radius equal to one of the values of a given by

$$a = \frac{\tau^2 h^2}{4\pi^2 m e E},$$

where $\tau^2 = 1, 4, 9, 16, 25, \dots$. Since a cannot undergo slight changes, there can be no oscillations in the plane of the orbit, and the circumstance, pointed out originally by Nicholson, that such oscillations would, on the old mechanics, be unstable, is no longer an objection. The normal hydrogen atom will be that in which the loss of energy has been greatest, and so is given by $\tau = 1$. On putting in numerical values, the diameter of the orbit is found to be given by $2a = 1.06 \times 10^{-8}$ cm., which is certainly of the right order of magnitude. But it is an essential part of Bohr's theory that there can be hydrogen atoms of sizes 4, 9, 16, 25, . . . times this.

37. The radius of the electron orbit of a particular atom is not supposed to be fixed for all time, and we have to consider the possibility of a sudden shrinkage from, say, the orbit given by $\tau = \tau_1$ to the orbit given by $\tau = \tau_2$. No suggestion is made by Bohr's theory as to what determines when this shrinkage shall take place, or how it happens, but the formulæ already obtained show that when it does happen the system must experience a loss of energy of amount δW given by

$$\delta W = W_{\tau_2} - W_{\tau_1} = \frac{2\pi^2 m e^2 E^2}{h^2} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right). \quad \dots \dots \dots (58)$$

Bohr supposes that the whole of this energy, suddenly set free from the atom, passes away into space in the form of absolutely monochromatic radiation. He further supposes that *the amount of this radiation is exactly one quantum*. Thus δW , given by equation (58), must be the same as ε in Planck's equation (38), and therefore equal to $h\nu$. It is also, of course, equal to the quantity $\varepsilon_m - \varepsilon_n$ in Einstein's equation (44), and so again equal to $h\nu$.*

The equation $\delta W = h\nu$, according to Bohr, determines the frequency of the monochromatic light emitted. Putting the right-hand of equation (58) equal to $h\nu$, the frequency is seen to be given by

$$\nu = N \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right). \quad \dots \dots \dots (59)$$

where

$$N = \frac{2\pi^2 m e^2 E^2}{h^3}. \quad \dots \dots \dots (60)$$

* Einstein's derivation of the radiation formula appeared subsequent to the appearance of Bohr's theory, being indeed framed with special reference to this theory.

According to Bohr's theory, the different values of τ_1 and τ_2 which can be inserted in this equation must give the frequencies of the different spectral lines of the substance. The lines can be sorted into series corresponding to different values of τ_2 . For instance, there will be a series given by $\tau_2=1$, and the lines of this series will be given by $\tau_1=2, 3, 4, \dots$; there will be a series $\tau_2=2$, with lines given by $\tau_1=3, 4, 5, \dots$; and so on.

38. *Hydrogen Spectrum*.—To obtain the hydrogen spectrum, we simply take $E=e$, and so

$$N = \frac{2\pi^2 m e^4}{h^3} \dots \dots \dots (61)$$

The series $\tau_2=2$ gives the series of lines

$$\nu = N \left(\frac{1}{4} - \frac{1}{n^2} \right), \quad (n=3, 4, 5, \dots)$$

and this is exactly the well-known Balmer's series. The numerical agreement is almost perfect, for on substituting the best-known values for m , e and h , namely, those of Bucherer and Millikan,*

$$\begin{aligned} e/m &= 1.767 \times 10^7 \\ e &= 4.774 \times 10^{-10} \\ h &= 6.545 \times 10^{-27}, \end{aligned}$$

equation (61) gives $N=3.294 \times 10^{15}$, whereas the spectroscopically determined value is $N=3.290 \times 10^{15}$, the error thus being well within the probable errors in the assumed values of e , m and h .

The value $\tau_2=1$ in equation (59) would give the series

$$\nu = N \left(1 - \frac{1}{n^2} \right), \quad (n=2, 3, 4, \dots),$$

all the lines of which would be in the extreme ultra-violet. None of the lines of this series had been observed when Bohr published his Paper, but the series was subsequently discovered by Lyman.†

The value $\tau_2=3$ gives the series

$$\nu = N \left(\frac{1}{9} - \frac{1}{n^2} \right), \quad (n=4, 5, 6).$$

This is commonly known as the Paschen series. Its first two lines ($n=4, 5$) were observed by Paschen‡ in 1908, and the next three ($n=6, 7, 8$) were observed by F. S. Brackett§ in 1922.

The value $\tau_2=4$ gives the series

$$\nu = N \left(\frac{1}{16} - \frac{1}{n^2} \right), \quad (n=5, 6, 7 \dots)$$

of which the first two lines, far in the infra-red, have also been observed by Brackett.||

* The Electron, p.210.

† Nature, Vol. 93, p. 314, May 7 (1914).

‡ Ann. d. Physik, 27, p. 565 (1908).

§ Nature, Vol. 109, p. 209, Feb. 16 (1922).

|| *L.c. ante.*

The series $\tau_2=5, 6, 7 \dots$ are so far in the infra-red as not yet to have been observed.

This completes the list of lines obtainable from formula (59), and it will be noticed that certain lines, formerly ascribed to hydrogen, have not been accounted for. Bohr suggested, and the suggestion subsequently received full experimental confirmation, that these missing lines are readily explained as belonging to helium.

39. *Helium Spectrum.*—For helium the nuclear charge E is $2e$, and in the neutral helium atom there are two electrons describing orbits. A helium atom with one positive charge will, however, have only one electron describing an orbit around a charge $2e$, so that the spectrum of such an atom ought to be obtained on putting $E=2e$ in equation (59). If we keep for N the value assigned to it in equation (61), this spectrum can be put in the form

$$\nu=4N\left(\frac{1}{\tau_2^2}-\frac{1}{\tau_1^2}\right)=N\left(\frac{1}{(\frac{1}{2}\tau_2)^2}-\frac{1}{(\frac{1}{2}\tau_1)^2}\right). \quad (62)$$

The series $\tau_2=1$ lies in the remote ultra-violet and has so far eluded observation. Two lines of the series $\tau_2=2$, also in the ultra-violet, have recently been discovered by Lyman.*

The series $\tau_2=3$ may be regarded as falling into two parts according as τ_1 is even or odd, being equivalent to the two series

$$\nu=N\left(\frac{4}{9}-\frac{1}{n^2}\right), \quad (n=2, 3, 4 \dots) \quad (63)$$

$$\nu=N\left(\frac{4}{9}-\frac{1}{(n+\frac{1}{2})^2}\right), \quad (n=2, 3, 4 \dots) \quad (64)$$

These two series were observed by Fowler† in 1912 in a mixture of hydrogen and helium. They were at first attributed to hydrogen, but after the appearance of Bohr's theory it was suspected that they might belong to the spectrum of ionised helium. All doubt has now been removed by their having been observed, first by E. J. Evans,‡ and subsequently by Paschen,§ in tubes from which all traces of hydrogen had been removed, and from which no traces of known hydrogen lines could be obtained.

The series $\tau_2=4$ may again be regarded as falling into two parts, according as τ_1 is odd or even, namely—

$$\nu=N\left(\frac{1}{4}-\frac{1}{n^2}\right), \quad \dots \quad (65)$$

$$\nu=N\left(\frac{1}{4}-\frac{1}{(n+\frac{1}{2})^2}\right), \quad \dots \quad (66)$$

The first of these is obviously Balmer's series, so that the lines of this series can be

* Nature, Vol. 104, p. 314 (1919).

† Monthly Notices R.A.S., 73, p. 62, Dec. (1912), and Phil. Trans., 214, p. 254, Ap. (1914).

‡ Phil. Mag., 29, p. 284 (1915).

§ Ann. d. Physik, 50, p. 901 (1916).

emitted by helium as well as by hydrogen. The second is the series observed by Pickering in the star ζ -Puppis in 1896.* This series was attributed by Pickering to hydrogen simply from the analogy, now seen to be inadequate, that the series (65) was emitted by hydrogen. In the ζ -Puppis spectrum, in point of fact, the series (65) is observed to be more intense than the series (66), presumably indicating that the source of light is a mixture of hydrogen and helium.

40. One point of interest in connection both with stellar and laboratory spectra may be noticed here. We have already calculated the diameter of the hydrogen atom (§ 36) to be 1.06×10^{-8} cm. in the state $\tau=1$, but have further seen that an atom in the general state defined by the integer τ will have a diameter equal to τ^2 times this—e.g., for $\tau=30$, the diameter will be approximately 10^{-5} cm.

In stellar spectra lines are observed which, on Bohr's theory, require the existence of atoms in states specified by large values of τ , and so which must be of great diameter. For instance, Pickering observed no fewer than 33 lines in the ζ -Puppis series (66), while Dyson† and Evershed‡ were able to identify 29 lines of the Balmer series (65) in the spectrum of the solar chromosphere. The twenty-ninth line in the Balmer series must, on Bohr's theory, be emitted by an atom jumping from the state $\tau_1=31$ to $\tau_2=2$, and in the state $\tau_1=31$ its diameter must be nearly 1,000 times that of the normal hydrogen atom, or about 1.02×10^{-5} cm. There is no difficulty in conceding that atoms having these huge diameters may exist either in the stars or in the solar chromosphere; there is no doubt that the pressures are in both cases very low, and it is quite conceivable that atoms of the inflated size required by Bohr's theory may exist without any occurrence of overcrowding.

The question of laboratory spectra is rather more difficult. In 1919 Merton and Nicholson§ observed the Balmer series down to its twelfth member ($\tau_1=14$) in hydrogen at a pressure of 41 mm. Now, hydrogen atoms in the state $\tau=14$ have a diameter of 2.08×10^{-6} cm., whereas the mean distance apart of atoms at 41 mm. pressure is only 1.0×10^{-6} cm. Superficially, at least, there would seem to be the difficulty that the packing of the atoms must have been so close as to preclude the possibility of atoms expanding to the state $\tau=14$. Fortunately, it seems probable that the difficulty is only superficial. The observed line was so excessively feeble that its explanation only needed an insignificant fraction of the total number of atoms present to be in the state $\tau=14$, and, moreover, on Bohr's theory, hydrogen atoms in this state, although of diameter 2.08×10^{-6} cm. in two out of the three directions in space, are of only infinitesimal diameter in the third direction, so that the volume occupied by a hydrogen atom, even in state $\tau=14$, is incomparably less than that of a cube of edge 10^{-6} cm., which is the average space available for an atom.

Further light was thrown on the matter by some experiments made by R. W. Wood.|| In these the Balmer series was observed down to its twentieth line, but it was noticed that as the pressure was gradually raised, the highest members of the series disappeared in succession, exactly as required by Bohr's theory.

* *Astrophysical Journal*, 4, p. 369 (1896), and 5, p. 92 (1897).

† *Proc. Roy. Soc.*, 68 A., p. 33 (1901).

‡ *Phil. Trans.*, 197 A., p. 381 (1901).

§ *Proc. Roy. Soc.*, 96 A., p. 112 (1919).

|| *Proc. Roy. Soc.*, 97 A., p. 455 (1921).

41. Our discussion of Bohr's theory has so far been limited by the assumption, made in § 35, that the mass M of the nucleus is very great compared with the mass m of the negative electron. Bohr has shown* that if the ratio m/M is not neglected, the value of N , the Rydberg constant, will no longer be given by equation (60), but by

$$N = \frac{2\pi^2 e^2 E^2}{h^3} \frac{mM}{M+m}. \quad (67)$$

Thus, if M_H denote the mass of the hydrogen nucleus, so that that of the helium nucleus is $4M_H$, the ratio of the two N 's for helium and hydrogen will no longer be precisely 4 to 1 ; its exact value will be

$$\frac{4}{M_H + \frac{1}{4}m} \quad ; \quad \frac{1}{M_H + m}.$$

From the observed ratio of the two N's, taken from the best measurements of the hydrogen and helium lines, Fowler† obtains for the ratio M_H/m the value 1,836, with a probable error of ± 12 . Subsequently Paschen,‡ allowing for the relativity correction and other refinements, obtained the value 1,843.7. These values are in extraordinarily good agreement with the values of M/m observed in other and more direct ways. The best direct value for their ratio is probably that of Millikan, namely, $M_H/m=1,845$.

The Continuous Spectrum of Hydrogen.

42. Starting from the head of the Balmer series, and extending indefinitely towards the ultra-violet, hydrogen shows a faint continuous spectrum, which has been observed both in the laboratory,[§] and in solar protuberances and planetary nebulae.|| This spectrum receives a simple explanation in terms of Bohr's theory, and also provides information of value.

The lines of the Balmer's series are produced by electrons falling into the orbit $\tau=2$ from exterior orbits $\tau=3, 4, \dots \infty$, the fall from the orbit $\tau=\infty$ providing the head of the series. Obviously then a continuous spectrum beyond this head can be produced by electrons falling into the orbit $\tau=2$ from orbits possessing more energy than the orbit $\tau=\infty$ —i.e., by free electrons moving with a total energy which is positive. Thus, on Bohr's theory, the continuous spectrum is emitted as a result of the capture of free electrons by a positively charged hydrogen nucleus; that is to say, by the ordinary process of re-combination.

The circumstance that the spectrum is, so far as is known, absolutely continuous shows that the free electrons must be moving before re-combination, with all possible amounts of kinetic energy. It suggests (in opposition to a theory which has been developed by Epstein^(†)) that free electrons move with any kinetic energy they please, and that the quantum-theory imposes no restrictions on their motion of the kind which we have seen that it imposes on bound electrons.

* Phil. Mag., 27, p. 509 (1914).

† Royal Society, Bakerian Lecture (1914).

† Ann. d. Phys., 50, p. 901 (1916).

Stark, Ann. d. Phys., 52, p. 255 (1917).

|| Evershed, Phil. Trans. R.S., 197 A, p. 399 (1901), and W. H. Wright, Lick Obs. Bulletin, No. 291 (1917).

† Ann. d. Phys., 50, p. 85 (1916).

43. This completes our discussion of the hydrogen and helium spectra. One other case in which Bohr's theory seems to be successful is that of the single electron rotating round a nucleus of charge $3e$. This atom, on Bohr's view, is the lithium atom with a double positive charge, and it ought to show spectral lines of frequencies

$$\nu = 9N \left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right).$$

The special value $\tau_1 = 6$ gives, in addition to lines coinciding with those of the Balmer series, a pair of series

$$\nu = N \left(\frac{1}{4} - \frac{1}{(m \pm \frac{1}{3})^2} \right), \quad (68)$$

some of the lines of which have been identified by Nicholson* in the spectra of the Wolf-Rayet stars.

44. In the cases we have discussed, the agreement between the predictions of Bohr's theory and spectroscopic observation is so complete that little doubt can be felt that the theory is founded on a very firm basis of truth. Nevertheless it will be noticed that the cases we have considered have all been those of systems consisting of two constituents only, a positive nucleus and a negative electron revolving around it. Attempts have naturally been made, both by Bohr and others, to extend the theory to more complex systems. In particular, reference may be made to attempts by Bohr himself† to give a general explanation of the series spectra of the elements. It must, however, be admitted that the results of these efforts, interesting and suggestive as they are, do not carry conviction of the same inevitable kind as those of the simpler problems we have already discussed. This implies no failure in Bohr's theory; it arises merely out of an essential difference in the two problems. In the case of the systems with two constituents so far considered, all the elements of the problem are known and the physical constants involved are known to a high degree of accuracy, so that Bohr's theory predicts a spectral formula in which every numerical quantity is fully known; there are no unknown or "adjustable" constants. Comparison with observation is accordingly simple and, when the theory is found to survive the test, extraordinarily convincing.

The case of the atom of, say, sodium is very different. No doubt the atom of sodium consists of a central nucleus of charge $11e$, with eleven negative electrons revolving round it; but the way in which the orbits of these electrons are arranged is still unknown to us. As a consequence, the theory can explain the sodium spectrum only in quite general terms, and the prediction, in terms of known physical constants, of the frequency of the spectral lines, which forms so arresting a feature of Bohr's discussion of the hydrogen spectrum, is perforce absent.

For this reason we shall not discuss the general question of the spectra of the elements in the present report. We shall, however, devote the remainder of the present chapter to the special problem of the X-ray spectra of the elements, since,

* Monthly Notices R.A.S., p. 382, March (1913).

† See especially "Ueber die Serienspektren der Elemente," *Zeitschrift für Physik*, 2, p. 423 (1920); or English translation in *The Theory of Spectra and Atomic Constitution*, by N. Bohr, Camb. Univ. Press (1923).

as will immediately be seen, these provide a very clear and convincing test of the validity of Bohr's theory of atomic structure.

THE X-RAY SPECTRA OF THE ELEMENTS.

45. When an element is suitably excited its atoms emit X-ray radiation, and the spectrum of this radiation consists of lines of definite frequency, analogous to the ordinary optical line-spectra.

In 1913 Moseley showed that the frequencies in the X-ray spectrum of any element satisfy a formula of the general type

$$\nu = N(n - \sigma)^2 \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right). \quad (69)$$

in which N is the ordinary Rydberg constant for hydrogen, of which we have found the value to be given by equation (61), τ_1, τ_2 are integers, n is a constant for any element, being in point of fact equal to the atomic number of the element, and σ is a quantity, always positive and small in comparison with n , which varies from one element to another, and also depends on τ_2 and τ_1 . If it were not for the limitation that σ is always positive and always small in comparison with n , the statement we have just made would be valueless, for if σ were entirely at our disposal, and free to depend, to any extent, on n, τ_1 and τ_2 , we could, of course, fit any observed series of lines into formula (69). Thus, the essence of the matter is the ascertained smallness of σ , and this immediately suggests an explanation of the X-ray spectrum.

If σ were equal to zero, Moseley's formula (69) for the frequencies of the X-ray spectrum would become

$$\nu = n^2 N \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right). \quad (70)$$

On substituting the value of N from equation (61) we find

$$n^2 N = \frac{2\tau^2 m e^2 E^2}{h^3},$$

where $E = ne$. Since n is the atomic member of the element in question, the nuclear charge of the atom will be ne , so that formula (70) represents, on Bohr's theory, the spectrum which would be emitted by systems in which single electrons described orbits about the central nuclei. Thus, when $n=1$ formula (70) gives the normal hydrogen spectrum, and when $n=2$ it gives the spectrum of positively charged helium. But in the case of elements for which n is large it cannot be supposed that such systems can have any real existence, and, moreover, σ is not strictly zero in equation (69). Moseley accordingly supposed that the presence of σ must represent the effect of the presence of the other negative electrons in the atom. This amounts to assuming that the force to the centre of the atom is $(n-\sigma)e/r^2$ in place of ne/r^2 . It does not seem necessary here to discuss the evaluation of σ in detail; our object is rather to point out that Bohr's theory has rendered signal service, and, incidentally, received striking confirmation in connection with X-ray spectroscopy. When we pass from optical spectra to X-ray spectra, in which the radiation is of from 1,000 to 100,000 times the frequency observed in optical spectra, the emission of radiation still appears to be governed by the dynamical principles discovered by Bohr.

We may here mention a further phenomenon which is not only important in itself, but is of interest as illustrating the wide applicability of the quantum-laws. When a stream of rapidly moving electrons all having the same velocity v impinge on a material target, the emitted X-radiation is found on analysis to yield a continuous spectrum, which is, however, limited perfectly sharply to frequencies below a certain critical frequency ν . This critical frequency was shown first by Duane and Hunt,* and then by Hull,† to be connected with the kinetic energy of the exciting electrons by the simple relation

$$\frac{1}{2}mv^2 = h\nu$$

where h is Planck's constant. This relation is believed to be strictly true for all kinds of matter and for X-radiation of all degrees of hardness.‡ When subsequently used by Blake and Duane§ and others for the exact determination of h this relation yielded the value

$$h = 6.555 \times 10^{-27}$$

which is in highly satisfactory agreement with the best known values of Planck's constant obtained by other methods (*cf.* §61 below).

The exact agreement between the value of h determined in this way and the value of Planck's constant makes it clear that the phenomenon must be in some way governed by quantum-dynamics, although the details are still far from clear. Sommerfeld|| has suggested that one must imagine the incident electron to penetrate only momentarily into an atomic structure and, after deflection by the nucleus, to shoot out in a hyperbolic orbit with its energy lessened as the result of the nuclear attraction, the dropped energy appearing as a single quantum of radiation of the appropriate frequency. The suggestion obviously gives a satisfactory explanation of the facts, but otherwise there is but little evidence either in its favour or against it. We notice that if the explanation is true, an accelerated electron which is not permanently bound to an atom must, as on the classical mechanics, radiate energy, but with the essential difference that the emission is now in complete quanta of monochromatic light. Moreover the same mechanism which causes fast-moving electrons passing through atoms to emit a continuous X-ray spectrum ought to cause the slower-moving "free" electrons in conductors to emit a continuous visible spectrum, in which case we need not go further afield for an explanation of the ordinary continuous black-body spectrum.

* Phys. Rev., 6, p. 166 (1915).

† Phys. Rev., 7, p. 157 (1916).

‡ For a fuller discussion of the continuous spectrum of the X-rays, see Duane's report, Bulletin of the National Research Council, 1, p. 383 (1920); or Sommerfeld, Atomic Structure and Spectral Lines, p. 177ff.

§ Phys. Rev., 10, p. 624 (1917).

|| "Atomic Structure and Spectral Lines," p. 450.

CHAPTER V.

THE PHOTO-ELECTRIC EFFECT AND THE ABSORPTION OF RADIATION.

46. A further striking instance of a phenomenon which entirely defies explanation in terms of the Newtonian mechanics, but yields immediately to the quantum-theory, is found in the "photo-electric" effect.

The general features of the phenomenon are well known. For many years it has been known that the incidence of high-frequency light on to the surface of a negatively charged conductor tended to precipitate a discharge, while Hertz showed that the incidence of the light on an uncharged conductor resulted in its acquiring a positive charge. These phenomena have been shown quite conclusively to depend on the emission of electrons from the surface of the metal, the electrons being set free in some way by the incidence of the light.

In any particular experiment, the velocities with which individual electrons leave the metal have all values from zero up to a certain maximum velocity v , which depends on the conditions of the particular experiment. No electron is found to leave the metal with a velocity greater than this maximum v . It seems probable that in any one experiment all the electrons are initially shot off with the same velocity v , but that those which come from a small distance below the surface lose part of their velocity in fighting their way out to the surface.

Leaving out of account such disturbing influences as films of impurities on the metallic surface, it appears to be a general law that the maximum velocity v depends only on the nature of the metal and on the *frequency* of the incident light. It does not depend on the *intensity* of the light, and within the range of temperature within which experiments are possible it does not depend on the temperature of the metal. The non-dependence on intensity was first established by Lenard,* and has subsequently been confirmed in an interesting way by Pohl and Pringsheim† and by Millikan,‡ who found that the maximum velocity was the same whether using either very intense spark-light, or arc light of the same wave length. And, as regards dependence on temperature, Ladenburg§ has examined the photo-electric effect for three metals (Au, Pt and Ir) up to 800°C., and found it independent of the temperature, while Lienhop|| has worked down to -180°C. with the same result.

For a given metal this maximum velocity increases regularly as the frequency of the light is increased, but there is a certain frequency, ν_0 , below which no emission takes place at all. For instance, for sodium, $\nu_0 = 5.15 \times 10^{14}$, which is the frequency for green light. Light more red than this can fall on sodium for centuries without producing any photo-electric effect at all.

* Ann. d. Phys., 8, p. 149 (1902).

† Verh. d. Deutsch. Phys. Gesell, 15, p. 974 (1912).

‡ Phys. Rev., 1, p. 73 (1913).

§ Verh. d. Deutsch. Phys. Gesell, 9, p. 165 (1907).

|| Ann. d. Phys., 21, p. 281 (1906).

must be equal to eV , where V is the ionisation potential of the substance in question. A comparison between the ionisation potential calculated in this way and that deduced more directly from observation provides yet another test for the theoretical explanation of equation (71). So far as the results go, they are favourable to the theory, but there is extreme difficulty in determining ionisation potentials directly with any high degree of accuracy.

48. It is worthy of notice* that this theory, which has been seen to give such a satisfactory explanation of the photo-electric effect, falls into place very naturally as a logical extension of Bohr's theory, which in the last chapter was seen to account for the observed phenomena of line spectra. The quantity $h\nu_0$ which has been used in this chapter is the amount of energy required to set the electron free, without velocity, from its orbit, and so is exactly equal to the quantity denoted by W in the last chapter. If we suppose W_1 to be the lost energy in the normal state, corresponding to $\tau=1$ in the last chapter, and W_∞ to be the lost energy in the state $\tau=\infty$, in which the electron is free at infinity, then $W_1=h\nu_0$ and $W_\infty=0$. Thus equation (71) may be written in the form

$$\begin{aligned} \frac{1}{2}mv^2 &= h\nu - h\nu_0 = h\nu - (W_1 - W_\infty) \\ \text{or} \quad h\nu &= W_1 - W_\infty + \frac{1}{2}mv^2 \quad \dots \dots \dots (72) \end{aligned}$$

Bohr's equation giving the line spectrum was (cf. equation (58))

$$h\nu = W_{\tau_2} - W_{\tau_1} \quad \dots \dots \dots (73)$$

This equation referred to the *emission* of radiation accompanying the shrinkage of the atom from the state τ_1 to the state τ_2 . The physical process must, however, be reversible, so that the incidence of a quantum of energy of frequency ν given by equation (73) on an atom in the state τ_2 ought to result in the absorption of the radiation and the expansion of the atom to the state τ_1 . Thus a line of this frequency ought to appear in the absorption spectrum of the gas, provided there are atoms in the gas in the state τ_2 ; if there are no atoms in this state, there would be no absorption of light of this frequency. For instance, in ordinary inert hydrogen there are presumably no atoms in the state $\tau_2=2$, so that the corresponding lines, which constitute the Balmer series, do not appear as absorption lines. In general, when atoms occur in an inert gas, they may all be expected to be in the final state in which $\tau=1$, so that the only lines of the emission spectrum which may be looked for in the absorption spectrum will be the lines given by $\tau_2=1$, namely, lines of frequency given by

$$h\nu = W_1 - W_n \dots (n=2, 3, 4, \dots \infty). \quad \dots \dots \dots (74)$$

If radiation of one of these frequencies falls on a gas it will be absorbed; if radiation of a frequency intermediate between these frequencies falls on a gas it will not be absorbed, for it could only be absorbed by complete quanta, and one quantum of energy would take the atom to a state intermediate between two of the states given by integral values of n , which is impossible. But if radiation of a frequency higher than the highest given by equation (74) (namely, that corresponding to $n=\infty$) falls on a gas it will be absorbed, for the absorption of one quantum will carry the atom beyond the state $n=\infty$, i.e., it will set one electron free altogether, and endow it in addition with kinetic energy of amount given by equation (72). This last

* See Bohr, Phil. Mag., 26, p. 17 (1913).

phenomenon is now seen to be simply the photo-electric effect, interpreted according to Einstein's theory; it is a necessary logical extension of Bohr's theory of absorption.

The complete absorption spectrum ought, according to this view, to consist of a series of lines given by taking $\tau_1=1$ in equation (59) and a continuous band stretching from $n=\infty$ (the head of this series of lines, given by $\nu=W_1/h$) up to $\nu=\infty$. In this spectrum the lines would represent the reversal of Bohr's emission effect, while the band would represent reversal of the continuous spectrum of the kind discussed in § 42, or, what is precisely the same thing, representing the photo-electric effect.

An hydrogen absorption spectrum of precisely this type has been observed in several stars,* although not in the laboratory. But in the laboratory R. W. Wood,† experimenting on the absorption spectrum of sodium vapour, has observed a complete absorption spectrum of exactly this type. Fifty lines were observed agreeing exactly in position with those of the principal sodium series, and in addition a continuous absorption beginning at the head of this series and extending to the extreme ultra-violet.

49. Perhaps the most striking confirmation of the general truth of the train of ideas just explained arises out of the development of an experimental method first employed by Franck and Hertz.‡ Their original experiments were devised to test the loss of energy, if any, at collisions between electrons and atoms. Electrons were projected with ever-increasing velocities into a mass of mercury vapour. At first it was found that the electrons rebounded from the mercury atoms without any loss of energy whatever, precisely as though the mercury atoms were perfectly elastic spheres. But as soon as a certain velocity of projection was reached, corresponding to a fall through a potential-difference of 4.9 volts, inelastic collisions began to occur; at the same instant the line λ 2537 of mercury was observed to appear. Now the frequency of this line is 1.1823×10^{15} , whence we readily calculate that the quantum $h\nu$ is equal to 7.745×10^{-12} erg, and this in turn is found to be the amount of energy gained by an electron in falling through a potential-difference of 4.86 volts. The connection between the excitation potential 4.9 volts and the wave-length of the emitted light is now obvious, and there can be but little doubt as to its physical interpretation. The mercury atom can exist only in certain definite states, corresponding to certain definite amounts of energy. Consequently the only amounts of energy which a mercury atom can absorb are the precise amounts required to change it from its present state to the various other possible states. If an electron strikes a mercury atom with less than the smallest of these amounts of energy, the mercury atom cannot absorb any of the electronic energy, so that a perfectly elastic collision takes place. But as soon as the electrons bring with them the smallest of these amounts of energy, the energy offered is such as can be accepted by the mercury atom. An inelastic collision accordingly takes place, the electron loses energy and the mercury atom is changed to a state of higher energy. The spon-

* J. Hartmann, *Phys. Zeits*, 18, p. 429 (1917).

† Cf. Bohr, *l.c.* p. 17, or Wood, *Physical Optics*, p. 513 (1911).

‡ The original Papers appear in the *Verh. d. Deutsch. Phys. Gesell.*, Vols. 15 et seq. A good general account of the results will be found in Sommerfeld's "Atomic Structure and Spectral Lines," p. 337, or in Gerlach's "Die Experimentellen Grundlagen der Quanten Theorie" (Braunschweig, 1921).

taneous return of the atoms to their original state will, in accordance with Bohr's ideas, be accompanied by the emission of monochromatic radiation of frequency such that the quantum is equal to the amount of energy initially received from each inelastic electron collision.

The general experimental method has been widely extended in various directions;* we need only mention the following :—It has been found by Horton and Davies, Rau and others that as the excitation voltage is gradually increased, the various lines of a spectral series flash out one after another. Finally, it has been found by Davis and Goucher and others that when the excitation voltage is such that the head of the series is reached, direct ionisation first occurs. For instance, the line λ 2537 of mercury is the first line of a series of which the head has a frequency for which the quantum has energy corresponding to 10.39 volts. Ionisation in mercury is found actually to occur at 10.4 volts.

The following table, compiled from material given in Sommerfeld's book, shows the agreement between observation and theory in the case of certain elements (alkalis and alkaline earths) :—

Element.	Excitation Potentials in Volts.		Ionisation Potentials in Volts.	
	Obs.	Calc.	Obs.	Calc.
Na.....	2.13	2.09	5.13	5.11
K	1.55	1.60	4.1	4.32
Rb.....	1.6	1.55	4.1	4.15
Cs.	1.48	1.38	3.9	3.87
Mg.....	2.65	2.7		
	4.42	4.33	7.75	7.61
Ca.	1.90	1.88		
	2.85	2.92	6.01	6.09
Zn.	4.1	4.01		
	5.65	5.77	9.3	9.5
Cd.	3.88	3.78		
	5.35	5.39	8.92	8.95
Hg.....	4.9	4.86		
	6.7	6.67	10.38	10.39

THE X-RAY PHOTO-ELECTRIC PHENOMENON.

50. Just as it is found that Bohr's conception of the emission of radiation is valid for radiation of all frequencies from the extreme infra-red to the hardest X-ray radiation, so also it is found that Einstein's conception of the photo-electric phenomenon is valid for radiation of all frequencies for which the phenomenon can be observed—i.e., from the yellow light at which the alkali metals are first affected up to the hardest X-rays.

In what is called the X-ray photo-electric phenomenon, X-rays of a known maximum frequency are generated by allowing electrons of known energy to strike a target (*cf.* § 45). When these X-rays in turn pass over matter, electrons are ejected with velocities which are found to conform exactly to Einstein's equation (71). There is, however, an essential difference between the application of the equation to visible light and to X-rays. The "threshold-frequency" ν_0 is such that

* For full details, *see* Sommerfeld, *l.c. ante.*

$h\nu_0$ is the energy required to detach an electron from an atom of the substance in question. When the photo-electric effect first comes into play ν is exactly equal to ν_0 , and for all the applications to visible light ν_0 is comparable with ν . But when we pass to X-radiation ν has a value equal to thousands of times its value for visible light, so that ν_0 is now insignificant in comparison with ν , and the equation assumes the approximate form

$$\frac{1}{2}mv^2 = h\nu.$$

This has the simple interpretation that the energy of the ejected electron is equal to that of a quantum of the incident X-radiation, and this in turn is equal, as we know, to the energy of the electrons which excited the X-radiation in the first instance.

There is an extension of this phenomenon of a kind which was not possible in the case of visible light. We have seen that to pull off an electron from an atom requires an expenditure of energy which is about equal to the quantum of energy for visible radiation. But after one electron has been pulled off others remain, and we can imagine the process of an atom being stripped of its electrons one by one until only the nucleus is left. As we pass further and further into the atom the energy required to detach an electron continually increases, that required to detach an electron from one of the inner shells being known to be of the order of magnitude of a quantum of X-radiation. Indeed, the limits of the X-ray spectrum of an element will, as we have seen (§ 45) be of frequencies such that the corresponding quanta represent the energies necessary to detach electrons from the inner shells—the so-called K and L rings. Thus if X-ray radiation is used to detach electrons from these inner shells, the velocity of the detached electron ought, according to the quantum theory, to be given by Einstein's equation (71) where ν is the frequency of the incident radiation and ν_0 is the frequency of the limit of the X-ray spectrum corresponding to the detachment of the electron in question.

De Broglie* by photographing the magnetic spectrum of the ejected electrons has been able to calculate their velocities of ejection. The spectrum is found to be a "line-spectrum," so that each electron is shot off with one or other of a definite series of velocities, and these velocities are found to be given precisely by equation (71) where ν_0 is the frequency of one or other of the limits of the X-ray spectrum.

Ellis† has applied a similar method to the electrons ejected by the γ -rays of radium B from the heavy elements Ur, Pb, Pt, W and Ba, and has obtained a similar result, except that in this case the frequencies of the exciting γ -radiations were unknown. Since, however, the frequencies ν_0 are known, it is possible to use equation (71) for the determination of ν . In this way Ellis calculated the frequencies of the γ radiation emitted by radium B, radium C and thorium D.‡ A discussion of the values obtained shows that it is very probable that the γ -rays of radioactive bodies are emitted from the nucleus. The constituents of the nucleus seem to be limited to a definite discrete series of configurations, the ejection of a γ -ray being caused by the step down from a configuration of higher energy to one of lower energy, so that even in the nucleus of an atom the principles of quantum-dynamics appear to hold sway.

* Comptes Rendus Nos. 5, 9, 12, Vol. 172 (1921), or "Les Rayons X," or Report to the 1921 Solvay Congress of Physics, published in "Atomes et Electrons."

† Proc. R. S., 99A, p. 261 (1921).

‡ Proc. R. S., 101A, p. 1 (1922).

CHAPTER VI.

THE SPECIFIC HEAT OF SOLIDS.

51. Still a further application of the fundamental principles of the quantum-theory is required for a satisfactory explanation of the specific heats of solids. According to the well-known law of Dulong and Petit, the product of the atomic weight and the specific heat of an element has, at least at ordinary temperatures, a value which is approximately the same for a great number of elements. This product is called the atomic heat, and is approximately equal to 5.95. A simple explanation of this law is provided by the usual kinetic theory of matter.

Suppose that 1 gramme of the substance in question contains N atoms, each of mass m , so that $Nm=1$. Let each atom have s degrees of freedom—that is to say, if all the other atoms are held at rest, let it be possible for each atom to have s entirely independent motions of its own. Then the expression for the energy of each atom will be that of the energy of s vibrations, and so it follows from the theorem of equipartition of energy (§ 16) that the average energy of each atom will be

$$sRT, \quad \dots \dots \dots (75)$$

where T is the absolute temperature, and the total energy E of the substance per gramme will be $NsRT$. The specific heat will be $\frac{\partial E}{\partial T}$ in energy units, or $\frac{1}{J} \frac{\partial E}{\partial T}$ in heat units, where J is the mechanical equivalent of heat. Calling this specific heat c , we have

$$c = \frac{1}{J} \frac{\partial E}{\partial T} = \frac{1}{J} \frac{\partial}{\partial T} (NsRT) = \frac{NsR}{J} \dots \dots \dots (76)$$

Let a be the atomic weight of the element, that of oxygen being taken to be 16. Then the mass of an atom m of the element is $am_0/16$, where m_0 is the mass of an atom of oxygen. For the oxygen atom, $R/m_0 = 520 \times 10^4$, so that for the element now under consideration

$$\frac{R}{m} = \frac{16}{a} \times 520 \times 10^4,$$

and since $Nm=1$, this is also the value of RN . The value of J is known to be 4.184×10^7 , so that equation (76) becomes

$$c = 1.98 \frac{s}{a}.$$

The constancy of ca , which is postulated by the law of Dulong and Petit, is seen now to depend simply on the constancy of s . Moreover, s must from its meaning be an integral number, and to give to the product ac the value required by Dulong and Petit's law we must obviously have $s=3$, giving $ac=5.95$.

Each atom must have a value of s at least equal to 3, for it has three independent motions in space—namely, those parallel to the axes of x , y and z . The observed

value of the product ac is thus accounted for by supposing that the atom has no further independent motions; from the point of view of specific heats the atoms are to be thought of as rigid points.

52. Just as in a gas, there is a distinction between specific heats at constant volume and at constant pressure, the difference between the two depending, of course, on the amount of work required to compress the heated solid back to the volume it occupied when unheated. The older experimental determinations of specific heats of solids were concerned with the specific heats at constant pressure, but recently Nernst and Lindemann* have shown how to correct such values so as to deduce the specific heat at constant volume. Now, it is to the specific heat at constant volume that the theoretical evaluation of § 51 refers. The constancy of ac ought only to be true if c represents the specific heat at constant volume.

In 1911 a series of determinations of specific heats were undertaken at Berlin by Nernst and his collaborators Lindemann, Koref and others,† these determinations covering the whole range of temperature available in the laboratory, and all being corrected so as to refer to specific heats at constant volume.‡

It was found that the product ac at sufficiently high temperatures approximated very closely to its theoretically predicted value 5.95, but that there was a very remarkable falling off at low temperatures. The accompanying figure will show the general nature of the results obtained. The curves give the atomic heats of four elements—lead, silver, aluminium, and carbon in the form of a diamond—the atomic heat being the ordinate and the absolute temperature being the abscissa. It is found that the curves of all the elements examined show zero atomic heat at absolute zero of temperature, and tend asymptotically towards the limiting atomic heat 5.95 as the temperature increases. A still more striking discovery is that all the curves are exactly similar, except for differences in the temperature scale. Thus, if we take the curve for silver and compress it horizontally in a certain ratio, which is about 1 : 2.3, it will be found to coincide exactly with the lead curve. Similarly, the aluminium curve, compressed in the ratio 1 : 1.8 would coincide with the silver curve, and compressed in the ratio 1 : 4.1 it would coincide with the lead curve.

53. The simple investigation of § 51 would apply equally at all temperatures if the fundamental principles on which it is based were sound. The principles on which the investigation was based were essentially those of the classical mechanics, so that the result of the experiments would seem to indicate that the principles of the classical mechanics are applicable at high temperatures but not at low. This is exactly the situation which, it was seen in § 31, might be expected to arise with regard to low-temperature phenomena. It is, therefore, natural to anticipate that the explanation of low-temperature specific heats is to be looked for in terms of the quantum-theory.

Explanations in terms of the quantum-theory, of great interest and suggestive-

* *Zeitschrift für Electrochem.*, p. 818 (1911).

† See especially Papers by Nernst, *Annalen der Physik*, 36, p. 395 (1911), and a report presented to the first Solvay Congress at Brussels, 1911, "*La Théorie du Rayonnement et les Quanta*," p. 254. Also Papers in the *Sitzungsberichte d. Preuss. Akad.* (1911), and in the *Zeitschrift für Electrochemie* (1911) and (1912).

‡ For the theory and details of this correction, see Nernst and Lindemann, *Zeitschrift für Electrochem.*, p. 817 (1911).

ness, were attempted by Einstein* and by Nernst and Lindemann.* Both of these had, however, a somewhat artificial element in them, and their importance lay rather in their paving the way for a final theory than in any claim to finality that they could profess. The explanation of the phenomenon, which, both from its complete naturalness and from its agreement with experiment, seems destined to be final, was given by Debye† in 1912.

54. In the analysis of § 51 we supposed each gramme of the matter under consideration to consist of N atoms, each having three degrees of freedom as though they were rigid points. There were $3N$ degrees of freedom in all, so that the total

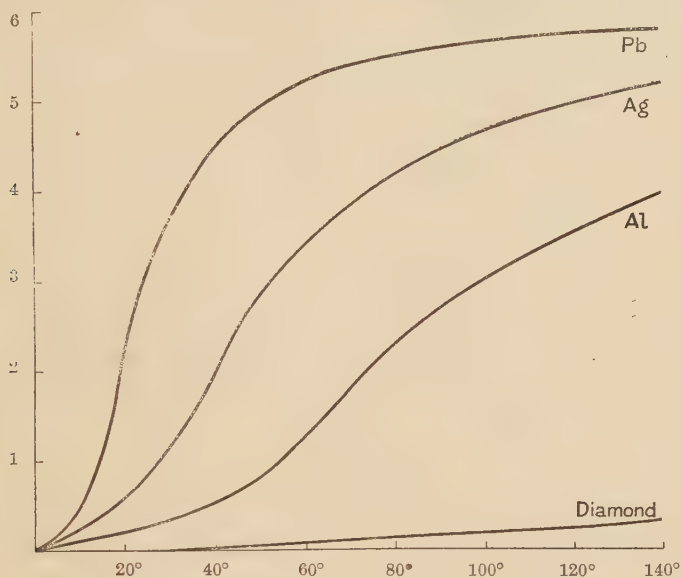


FIG. 2.

energy_{av} was, according to the older mechanics, $3NRT$, regardless of the particular nature or properties of these degrees of freedom. But according to the quantum-theory the average energy of a degree of freedom is not entirely independent of its nature; in the case of a vibration the average energy depends on the frequency of the vibration.

The atoms of the solid do not, of course, possess independent separate free vibrations. The oscillation of any one will set its neighbours into oscillation, and the free vibrations of the system are those of all the atoms simultaneously. But any motion, no matter how complicated, of the atoms can be analysed into trains of waves, just as was the case with the motion of the molecules of a gas in § 5. The number of independent vibrations of wave-length between λ and $\lambda+d\lambda$ has been

* The best account of these will be found in the reports of the first Solvay Congress at Brussels (1911), "*La Théorie du Rayonnement et les Quanta*" (1912), pp. 254, 407, in which will be found valuable discussions of the general problem. The theory of Einstein is explained later in the present report (§ 59).

† Zur Theorie der Spezifischen Wärmen, *Annalen der Physik*, 39, p. 789 (1912).

seen (§ 14) to be $12\pi\lambda^{-4}d\lambda$. Of these vibrations two-thirds are waves of distortion and one-third are waves of compression. Let the former be supposed propagated with velocity V_1 and the latter with velocity V_2 , then the frequencies of the former vibrations are V_1/λ and of the latter V_2/λ . It readily follows that the total number of vibrations with frequencies between ν and $\nu+d\nu$ is

$$4\pi(2V_1^{-3}+V_2^{-3})\nu^2d\nu \quad . \quad . \quad . \quad . \quad . \quad (77)$$

There must be a limit to the values of ν possible; obviously the formula breaks down when we come to frequencies such that the wave-length is comparable with the distance between adjoining atoms. Debye assumes, as an approximation, that formula (77) is true from $\nu=0$ up to a value ν_m , which is the maximum of all the frequencies, and is determined by the condition that the total number of degrees of freedom obtained by this assumption is equal to the known total number $3N$. In other words, we must have

$$3N=4\pi(2V_1^{-3}+V_2^{-3})\int_0^{\nu_m}\nu^2d\nu=\frac{4\pi}{3}(2V_1^{-3}+V_2^{-3})\nu_m^3, \quad . \quad . \quad . \quad . \quad . \quad (78)$$

and formula (77) may be replaced by

$$9N\frac{\nu^2d\nu}{\nu_m^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (79)$$

Debye proceeds by supposing that the energy of these vibrations is equal to the amount assigned to them by the quantum-theory as developed in § 22 of the present report. That is to say, each vibration of frequency ν is supposed to have an average amount of energy

$$RT \times \frac{x}{e^x-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (80)$$

where x stands as before for $\frac{h\nu}{RT}$. Thus the total energy of the solid, obtained by integrating over vibrations of all frequencies, is

$$E=\int_0^{\nu_m} 9NRT \frac{x}{e^x-1} \frac{\nu^2d\nu}{\nu_m^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (81)$$

Incidentally, it may be noticed that, according to the classical mechanics, we should have omitted the factor $\frac{x}{e^x-1}$ in (80), so that the total energy would have been

$$\int_0^{\nu_m} 9NRT \frac{\nu^2d\nu}{\nu_m^3} = 3NRT,$$

leading back at once to the result obtained in § 51, namely, that the atomic heat ought to have the value 5.95 at all temperatures.

On replacing x by $h\nu/RT$, the value of E given by formula (81) reduces to

$$E=\int_0^{\nu_m} \frac{9Nh\nu^3d\nu}{\nu_m^3(e^{h\nu/RT}-1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (82)$$

The integral unfortunately cannot be evaluated in finite terms. Details of its

numerical treatment and computations will be found in Debye's Paper already referred to.

A detailed statement of its agreement with experiment will be found in the same Paper. For the purposes of the present report the following instances will perhaps suffice.

55. According to equation (82) the various specific heat curves ought to be dependent only on a single parameter, and this may conveniently be taken to be a quantity Θ defined by

$$\Theta = \frac{h\nu_m}{R}. \quad \dots \dots \dots (83)$$

It is then easily seen that the specific heat at any temperature T ought to be of the form $f\left(\frac{\Theta}{T}\right)$, where f is a function of $\frac{\Theta}{T}$ which is the same for all substances. In Fig. 3, which is taken from Debye's Paper,* the continuous curve represents

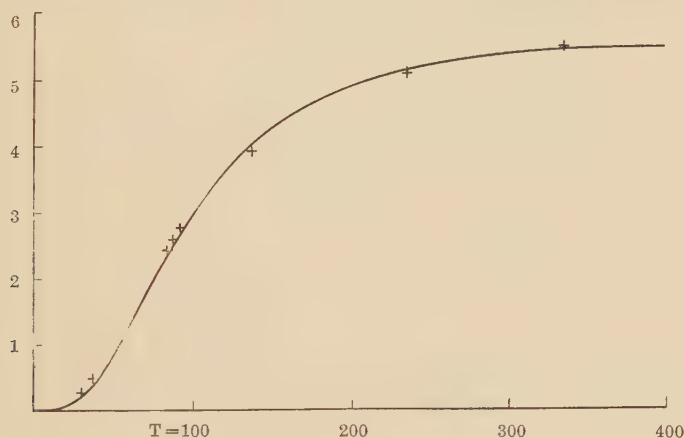


FIG. 3.

the graph of $f\left(\frac{\Theta}{T}\right)$ calculated from the integral (82), the scale of abscissæ being arranged for the value $\Theta=396^\circ$. The crosses represent the actually observed values of the specific heat for aluminium.

This figure accordingly exhibits the agreement between theory and experiment in the case of aluminium, provided that Θ , in the theoretical formula, is treated as an adjustable constant. The value of Θ for any particular substance, however, depends on ν_m , which is given by equation (78), and so admits of calculation when the elastic constants of the substance are known. The following comparison is given by Debye between observed and calculated values of Θ :—

Element.	Θ observed.	Θ calculated.
Al	396	399
Cu	309	329
Ag	215	212
Pb	95	72

* *L.c.*, p. 812.

In these comparisons, the value of “ Θ observed” is obtained by fitting a curve of the type predicted by theory to the observations as closely as possible, as, for instance, has been done for aluminium in Fig. 3.

56. Subsequent to the appearance of Debye's Paper, experiments on the specific heats of copper at temperatures only slightly above absolute zero, by Keesom and Kamerlingh Onnes,* have shown a much higher concordance between theory and observation than that shown in the preceding table.

In the limit when T is very small, the exponential $e^{h\nu/RT}$ in equation (82) becomes very large except when ν is small, so that, in this special case, the whole value of E comes from the contributions to the integral on the right-hand of equation (82) which are made by small values of ν . The value of E is accordingly the same as though the integral extended from $\nu=0$ to $\nu=\infty$, in which case it becomes integrable, and gives

$$\begin{aligned} E &= \int_0^\infty \frac{9N h \nu^3}{v_m^3} \left[e^{-h\nu/RT} + e^{-2h\nu/RT} + e^{-3h\nu/RT} + \dots \right] d\nu \\ &= 9N \frac{(RT)^4}{(h\nu_m)^3} \left(1 + \frac{1}{2^4} + \frac{1}{3^4} + \dots \right) \\ &= 9N \frac{(RT)^4}{(h\nu_m)^3} \times 6.495 \end{aligned}$$

whence we readily find that the specific heat at constant volume C_v is given by

$$C_v = 77.94 \left(\frac{T}{\Theta} \right)^3 C_\infty \dots \dots \dots (84)$$

where C_∞ is the value of C_v at infinite temperature.

At the lowest temperatures, then, Debye's theory predicts that C_v must vary as T^3 . The experiments of Keesom and Kamerlingh Onnes not only test this part of the theory, but enable us to test the general theory by comparing their observed value of Θ with that deduced from the elastic constants. Their observed values of C_v and of Θ , calculated from equation (84), are as follows:—

T	C_v	Θ
14.51	0.0396	329.6
15.59	0.0506	326.3
17.17	0.0687	324.6

The constancy of the values of Θ in the last column shows that C_v varies very closely as T^3 at low temperatures, while the mean of these values of Θ , namely, 326.8, is in excellent agreement with the values $\Theta=329$ calculated from the known elastic constants of copper.

57. These instances will have given some idea of the agreement between Debye's theory and observation. The agreement could not be expected to be perfect, for Debye's assumption of the existence of a sharply defined maximum frequency ν_m is obviously at best only a somewhat rough approximation. Various attempts have been made to improve Debye's theory in this respect; in particular, attention may be called to Papers by Born and Kármán,† in which the arrangement of atoms

* Verslag Amsterdam Akad., p. 335, June 26 (1915); or communications from the Physical Laboratory of Leiden, No. 147a.

† Physikalische Zeitschrift, 14, pp. 15 and 65 (1913)

in the solid is treated as forming a "space-lattice" of the type with which the work of Bragg on the theory of X-ray spectra has made us familiar.* The results obtained in this way agree, perhaps, somewhat better with experiment than those obtained with the simpler theory, but it seems probable that nothing short of a complete knowledge of the structure of matter will result in any very substantial improvement on Debye's formula.

According to Debye's theory, the solid itself must have free vibrations of frequencies ranging from 0 to the maximum frequency ν_m . The law of distribution of these frequencies is given by formula (79), showing that the number within a given small range $d\nu$ is proportional to $\nu^2 d\nu$. Thus the spectrum of these frequencies would be a band having its head at frequency ν_m , and falling off in intensity towards the low-frequency end. The value of ν_m can be calculated from the elastic constants of the solid by formula (78), and is found to be generally of the order of 10^{12} .

It will be noticed that this formula is derived theoretically by laying great stress on just that part of Debye's theory which is obviously most imperfect, namely, the supposition that the vibrations of the solid fall off absolutely suddenly at a certain frequency ν_m . It is, therefore, hardly to be expected that the values of ν_m calculated from it should agree exactly with the values determined from observation of the specific heat. Perhaps the most that can be expected is that the two sets of values should be approximately the same. This they may certainly be said to be, as will appear in the next section (*cf.*, table below).

58. Lindemann† has given the following formula, to some extent empirical, which is found to give the values of ν_m with surprising accuracy for the substances examined. If T_s denotes the melting point of the substance in degrees absolute, m the atomic weight and V the atomic volume, Lindemann's formula‡ is:—

$$\nu_m = 3.08 \times 10^{12} \times \sqrt{\frac{T_s}{mV^{\frac{1}{3}}}} \quad \dots \dots \dots (85)$$

This agrees rather better with the observed values of ν_m than do the values calculated directly from the elastic constants, as the table below shows§:—

Element.	ν_m calculated (Lindemann).	ν_m observed (spec. heats).	ν_m calculated (elastic constants).
Al	8.3×10^{12}	8.3×10^{12}	8.0×10^{12}
Cu	7.5×10^{12}	6.6×10^{12}	6.6×10^{12}
Zn	4.8×10^{12}	4.8×10^{12}	...
Ag	4.8×10^{12}	4.5×10^{12}	4.3×10^{12}
Pb	2.0×10^{12}	1.9×10^{12}	1.44×10^{12}
Diamond ...	35.0×10^{12}	40.0×10^{12}	...

* See also a Paper by H. Thirring, *Phys. Zeitsch.*, 14, p. 867 (1913), and also § 60 below.

† *Physikalische Zeitschrift*, 11, p. 609 (1910).

‡ In Lindemann's original Paper the multiplying constant, which is purely empirical, was taken to be 2.06×10^{12} and ν_m had a slightly different meaning.

§ In this table the first two columns are taken from the report by Nernst in "Vorträge über die Kinetische Theorie der Materie," p. 77 (1914), and are calculated by giving Lindemann's formula the form (69). Einstein takes the multiplying factor in Lindemann's formula to be 2.12×10^{12} , and a table of values calculated in this way is given by him in "La Théorie du Rayonnement et les Quanta," p. 415.

(85), and the correction term is calculated from the known physico-chemical constants of potassium chloride. Thus the calculated values in the fifth column are in reality derived from a formula in which every constant is evaluated by experiment, and there are no adjustable constants at all. Under these circumstances the agreement between the observed and calculated values of $2c_p$ must be regarded as very remarkable, the more so in view of the fact that equally good agreement is obtained in the case of other substances for which ν_2 (the frequency of the rest-strahlen absorption band) is known—namely, NaCl, AgCl, KBr and PbCl₂.

Values of $2c_p$ for KCl.

T.	Einstein term in $2c_v$.	Debye term in $2c_v$.	Correction term $2(c_p - c_v)$.	Calculated $2c_p$.	Observed $2c_p$.
22.8	0.046	1.04	...	1.086	1.16
26.9	0.13	1.48	...	1.61	1.52
30.1	0.25	1.87	...	2.12	1.96
33.7	0.43	2.25	...	2.68	2.50
48.3	1.43	3.52	...	4.95	5.70
57.6	2.13	4.06	0.02	6.21	6.12
70.0	2.89	4.57	0.04	7.50	7.58
86.0	3.66	4.97	0.06	8.79	8.72
235	5.55	5.81	0.32	11.68	11.78
416	5.83	5.91	0.68	12.42	12.72
550	5.87	5.93	0.90	12.70	13.18

Thus it will be seen that the quantum-theory is able to predict with striking success a relation between phenomena as different in their nature as black-body radiation, the principal infra-red absorption bands of solids, and their specific heats.

An attempt has also been made by Thirring* to account for the specific heats of compounds by extending the ideas of Born and Karman† to space lattices in which two or more different masses are supposed to alternate. In this way it is found possible to calculate the relation between the elasticity and specific heat for regular crystals. The calculation is carried out for NaCl, KCl, CaF₂ and FeS₂. The author finds a mean deviation of 2.3 per cent., with a maximum of 4 per cent. from observed values through the range of temperature considered by him, a range much less than that covered by Nernst's tables.

60. There is no doubt that there must, in theory at least, be other contributions to the specific heat besides those we have been considering; what is remarkable is that the corresponding deviations from the theoretical formulæ we have had under consideration seem to be hardly noticeable experimentally. The presence of free electrons must add something to the specific heat, but it appears as though the contribution were too small to be detected experimentally. Nernst and Lindemann have found no general difference between the specific heats of good and bad conductors; Richter‡ has examined the specific heats of a series of Bi-Sn and

* Phys. Zeitschr., 15, p. 180, and also p. 127 (1914).

† See above, § 56.

‡ Ann. d. Physik, 39, p. 1590 (1912).

Bi-Pb alloys with special reference to this question, and concludes that, in these alloys at all events, the free electrons do not contribute sensibly to the specific heat.

Again, the rotations of the atoms or molecules must in theory contribute something to the specific heats. The atoms certainly can rotate, for if a crystal is rotated in the hand its optical axes will be found to have rotated with the body as a whole, showing that each atom must have individually changed its direction; also if a magnet is turned, its magnetic field will turn with it. The absence of a noticeable contribution to the specific heats is accounted for, on the quantum-theory, by supposing that the forces opposing rotational movements of the atoms inside the solid are so large that the corresponding vibrations are of very high frequency, and so normally possess very little energy. As far as pure theory goes, there is no question that to the terms in the specific heat contemplated by Nernst's theory (§ 59) there ought to be added an additional term, of a form exactly similar to the Einstein term, but having $x = \frac{h\nu_3}{RT}$ where ν_3 is the frequency (or average frequency) of the vibrations which depend on the rotation of the atoms.*

It is worthy of notice that sodium and mercury show an increase in the specific heats, beyond that accounted for by the theories we have considered, as the fusion-point is approached,† when presumably the intensity of the forces which prevent the atom from rotating is relaxed; and Nernst and Lindemann find that in general the same is true for the substances they have examined.

But in normal cases these deviations from the simple theory are too small to be detected experimentally, and it may be stated as a general rule (not applicable close to the fusion-point) that the motion of translation of the atoms suffices to account for the observed specific heats.

61. Debye's result (§§ 54, 55) may be summarised in the statement that the whole heat-energy of an element resides in the energy of its elastic-solid vibrations, the atoms being treated as the particles of the solid, and each vibration having exactly the energy allotted to it by the quantum-theory. Nernst has shown that for the compounds examined by him the same is true except that the molecules must be treated as the particles of the solid, and to the energy of the elastic vibrations of the solid must be added the energy of the internal vibrations of the molecules, each vibration again having exactly the energy allotted to it by the quantum-theory.

Both these theories, as well as the theories of Born and Karman, and of Thirring, are covered by a general explanation that the heat-energy of a solid is the energy of the vibrations of the atoms of the solid, each vibration having exactly the energy allotted to it by the quantum-theory, and therefore having the same energy as a light vibration of identical frequency.

This recalls the result obtained in § 9, that the condition for equilibrium between a material vibration and light vibrations in the ether is the equality of mean energy of vibrations of the same frequency. This result was, in § 9, obtained from the old mechanics: the specific heat phenomenon suggests that it must be true in the quantum-mechanics also.

* See Grüneisen, *Molekulartheorie der Festen Körper*, report presented to the second Solvay Congress of Physics (Brussels, 1913), also A. E. Oxley, *Proc. Camb. Phil. Soc.*, 17, p. 450 (1914).

† Oxley, *l.c.*

CHAPTER VII.

THE DYNAMICS OF THE QUANTUM-THEORY.

62. We have now briefly discussed the four phenomena which give the most direct evidence of the failure of the classical dynamics and of the need for a new system of dynamics which we may term quantum-dynamics. The four phenomena that we have had under consideration have been—

- (i.) Black body radiation.
- (ii.) The spectra of the elements
- (iii.) The photo-electric effect.
- (iv.) The specific heats of solids.

That the phenomena agree in showing the inadequacy of the Newtonian mechanics will need no further argument ; that they agree in pointing to the same new system of quantum-dynamics will become clear on comparing the values of h which are deduced from the four phenomena in question. These values are as follows :—

(i.)	From black-body radiation*	$h=6.55 \times 10^{-27}$
(ii.)	From Rydberg's constant†	$h=6.547 \times 10^{-27}$
	From K-ray spectra‡	$h=6.555 \times 10^{-27}$
(iii.)	Photo-electric effect (sodium)§	$h=6.561 \times 10^{-27}$
	(lithium)	$h=6.585 \times 10^{-27}$
(iv.)	Specific heats at low temperatures¶	$h=6.59 \times 10^{-27}$

Thus the same constant h appears as being intimately connected with all the four phenomena, which we have found the old mechanics unable to explain. What is h , and what is the new dynamics which appears to centre round its existence ?

We found that the phenomenon of black-body radiation could be explained if we assumed that radiant energy existed only in complete quanta ε , defined by $\varepsilon=h\nu$, where ν is the frequency of the radiation ; or if we assumed (with Planck) that the energy of matter consisted wholly of energy of isochronous vibrators, and that the energy of each vibrator occurred only in complete quanta of energy ε , again defined by $\varepsilon=h\nu$, where ν is now the frequency of the vibrator ; or if we assumed (with Einstein) that atoms of matter could exist only in a certain series of definite states and that the transfer of energy between matter and the surrounding field of radiation, produced by the sudden jump of an atom from one state to another, occurred only by single complete quanta of the radiant energy, these quanta again being defined by the equation $\varepsilon=h\nu$.

Turning next to the line spectra of the simplest elements, we found that these

* W. W. Coblentz, Scientific Papers, Bureau of Standards, No. 360 (1920).

† R. A. Millikan, Phil. Mag., 34, p. 15 (1917).

‡ Blake and Duane, Phys. Review, 10, p. 624 (1917).

§ R. A. Millikan, Phys. Review, 4, p. 73 (1914).

|| R. A. Millikan, Phys. Review, 6, p. 55 (1915).

¶ From experiments of Keesom and Kamerlingh-Onnes (*cf.* § 56 of the present Report).

principle" of Ritz,* according to which all the series lines in the spectrum of an element have frequencies which can be expressed as differences of other frequencies. To take, for instance, the spectrum of hydrogen; if we write

$$v_s = \frac{N}{\tau_s^2} (88)$$

where N is the Rydberg constant, and τ_s is any integer from 1 to ∞ ; then the whole spectrum of hydrogen, as we have seen in Chapter IV., is obtained by putting

[illegible]

where m, n have all possible integral values from 1 to ∞ . In general, the spectrum of any element shows frequencies which can be expressed as simple differences of more fundamental frequencies in the manner of equation (89).

The truth and exactness of the combination principle are undisputed. The quantum hypothesis expressed in equation (87) requires us to suppose that radiation is emitted and absorbed in finite chunks, and the principle of conservation of energy now requires that either emission or absorption shall be accompanied by finite jumps in the energy of the material system which emits or absorbs energy. If we put

$$W_m = h\nu_m, \quad W_n = h\nu_n, \text{ etc.,}$$

so that W_m, W_n, \dots have the physical dimensions of energy, the combination principle expressed in equation (89) may be put in the form

$$h\nu = W_m - W_n$$

and the quantum hypothesis (87) now assumes the form

$$\Delta W = W_m - W_n.$$

In words, this equation shows that all possible jumps of energy in the radiation-emitting or radiation-absorbing mechanism may be expressed as simple differences of certain more fundamental energies $W_1, W_2, \dots W_m, W_n, \dots$. It would be difficult to interpret this in any more natural way than by supposing that the mechanism can exist only in certain definite states corresponding to energies W_1, W_2, \dots . The quantum-hypotheses which have been labelled (i.) and (iv.) confirm us in this interpretation, amounting indeed merely to special cases of the general result to which the combination principle has led us. Hypothesis (i.) requires that the possible states of an atom consisting of a nucleus and only one electron shall be specified by

[illegible]

while hypothesis (iv.) requires that the possible states of vibrations of an elastic solid shall be specified by

[illegible]

64. It is natural to inquire at this stage whether the special hypotheses expressed by equations (90) and (91) can be regarded as special cases of a single more general

* Phys. Zeitschr., 9, p. 521 (1908), or Astrophys. Journ., 28, p. 237 (1908). For a simple discussion see N. Campbell, "Series Spectra" (Camb. Univ. Press, 1921), p. 11. See also Fowler, "Report on Series in Line Spectra," p. 23.

of an elastic solid. Obviously, however, this cannot be the most general form of quantum-equation, for ν has no meaning, and \bar{T} has not been defined, except in reference to systems which repeat their configuration after definite isochronous intervals, each equal to $1/\nu$.

Adiabatic Invariants.

66. The number of functions which can be placed on the left hand of an equation such as (94) is strictly limited, for, as we shall now see, these functions must satisfy a very definite condition.

Let F be such a quantity, and let a dynamical system be describing a motion which conforms to the equation

[illegible]

where τ is an integer. Let one of the quantities which specify the strength of an external field of force acting on the system be slowly and gradually changed—for example, let us slowly and gradually create an electrostatic field in the neighbourhood of the system, or create, increase or diminish a magnetic field, or slowly and gradually introduce or remove a mechanical constraint. Let a be the quantity which gradually changes; then as a changes the motion of the system also will, in general, gradually change. Let a change slowly and gradually to a value $a + \delta a$ and then remain constant at this value. As the system follows the changes in a , the value of F will gradually change until at the end of the change it has a value which may be expressed symbolically as

$$F_0 + \frac{\partial a}{\partial F} \delta a$$

where F_0 is the initial value of F , which we have already supposed to be τh . Now, in order that equation (95) may be a possible quantum-equation in the general case in which a may have any value whatever, the final value of F , which is

$$F = \tau h + \frac{\partial F}{\partial a} \delta a,$$

must be of the form $\tau'h$, where τ' is an integer, and since this must be true for all values of δa , we must have

[illegible]

In words: *when the parameters which specify the strength or condition of an external field of force gradually change, F must remain unchanged in value.*

Following Einstein, Ehrenfest and Burgers, to whom the development of this train of thought is due, we speak of a function F which satisfies this condition as an "adiabatic invariant." We have seen that only "adiabatic invariants" can figure as the left-hand members of quantum-equations such as (95).

67. It is accordingly very significant that the function $2T/v$ which occupies the left-hand side of equation (94) is already known to be an "adiabatic invariant." This was proved by Boltzmann* in 1876, long before it was suspected that the result would be of any interest in molecular physics; recently slightly modified

* Vorlesungen über Mechanik, II., § 48.

proofs have been given by Ehrenfest* and Bohr†. Not only is the function an "adiabatic invariant," but it is the only function which is known to be an "adiabatic invariant" for all mechanical systems regardless of their special configuration or other properties. In special problems, or under special conditions, other functions may also be "adiabatic invariants"; examples given by Ehrenfest‡ are provided by a system possessing cyclic co-ordinates, in which case the corresponding momenta are "adiabatic invariants," and by a particle of any kind describing an orbit about a central field of force of varying intensity, in which case the moment of momentum is an "adiabatic invariant."

In the case of the Bohr atom it will be found that the angular momentum is equal to $2\bar{T}/\nu$ divided by 2π . Thus, as first pointed out by Nicholson, the quantum restriction for a Bohr atom can be expressed in the form that the angular momentum must be an integral multiple of $h/2\pi$. But the fact that $2T/\nu$ is a universal "adiabatic invariant," while the angular momentum is not, indicates that the most significant expression is that provided by equation (94).

68. The "adiabatic invariant" $2\bar{T}/\nu$ has reference only to systems for which the motion repeats itself after definite equal intervals $1/\nu$, for the symbol ν has no meaning except with reference to such systems. If we write σ for $1/\nu$, the period of the motion, we may put

$$\frac{2\bar{T}}{\nu} = 2\bar{T}\sigma = \int_0^\sigma 2T dt \quad (97)$$

since \bar{T} is by definition equal to the value of T averaged through a time-interval σ . This last integral is, of course, the "action" taken over a complete period. Thus while the Newtonian mechanics requires that the action shall be a minimum, the quantum-dynamics imposes the further restriction that the action, taken over a complete period in the special case now under consideration, shall be a multiple of h .

69. Consider for the moment the most general dynamical system specified by n generalised co-ordinates q_1, q_2, \dots, q_n and their rates of change $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_n$. Let E denote the total energy of the system, expressed as a function of $q_1, q_2, \dots, q_n, \dot{q}_1, \dot{q}_2, \dots, \dot{q}_n$, and let momenta p_1, p_2, \dots, p_n be introduced, defined by

$$p_s = \frac{\partial E}{\partial \dot{q}_s}, \text{ etc.}$$

Since the kinetic energy T is a quadratic function of the velocities, $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_n$, we have

$$2T = \sum \frac{\partial T}{\partial \dot{q}_s} \dot{q}_s = \sum \frac{\partial E}{\partial \dot{q}_s} \dot{q}_s = \sum p_s \dot{q}_s,$$

so that the action, taken over any time-interval 0 to t , is

$$\int_0^t 2T dt = \sum \int_0^t p_s \dot{q}_s dt = \sum \int_0^t p_s dq_s \quad (98)$$

* Verslag Amsterdam Acad., 25, p. 412 (1916).

† On the Quantum Theory of Line Spectra, Kgl. Danske Selsk. Skrifter, Naturvidoog Mathemat., 8, 4, I., p. 10 (1918).

‡ Phil. Mag., 33, p. 504 (1917).

70. In the special case in which the system has only one degree of freedom and a definite period σ , the generalised space of the type we introduced in §15 contains only two co-ordinates p and q and so reduces to a plane, while from equations (97) and (98)

$$\frac{2T}{\nu} = \int_0^\sigma p dq \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (99)$$

Also by hypothesis the point in this plane which represents the motion of the system returns to its original position at successive intervals σ , and so repeatedly describes a certain closed curve in this plane. The area of this closed curve is, of course, $\int p dq$, so that equation (99) shows that the complete area of the curve is equal to $2\bar{T}/\nu$. The quantum-restriction (94) which has been found to give accurate results in the problems of the Bohr atom and of the vibrations of an elastic solid is now found to assume the form

$$\int p dq = \tau h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (100)$$

Thus the effect of the quantum-restrictions is to limit the representative point to describing certain definite closed curves in the p, q plane, these curves being defined by the condition that their areas are integral multiples of h .

71. The discovery of suitable generalisations of equation (100) constitutes one of the principal problems of quantum-dynamics. In the most general case to which this equation is applicable, namely, a system of two degrees of freedom describing a recurrent motion with period σ , it is highly probable, although not yet rigorously proved, that the equation expresses the true quantum-equation of restriction. For the left-hand member is an "adiabatic invariant" and is the only known "adiabatic invariant" which leads to the right result in the simple cases of the Bohr atom and the vibrations of an elastic solid.

72. In certain dynamical systems the total energy E can be put in the form

$$E = f_1(p_1, q_1) + f_2(p_2, q_2) + \dots + f_n(p_n, q_n) \quad . \quad . \quad . \quad . \quad . \quad (101)$$

The motion of such systems, when calculated by the classical mechanics, is such that the changes in any one co-ordinate q_s are not affected by the values of the remaining co-ordinates q_1, q_2, \dots . For certain of those co-ordinates the motion will be recurrent, having a definite period which is, of course, independent of the motions of the other co-ordinates. The kinetic energy $2T$ of the system must, like E , fall into the sum of a number of separate contributions, one from each of the co-ordinates and its corresponding velocity. Now if q_s is any one co-ordinate, of which the corresponding motion has a period σ_s , and if T_s is the part of the kinetic energy which depends on q_s and p_s , it can be shown that

$$\int_0^{\sigma_s} 2T_s dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (102)$$

is an adiabatic invariant provided that none of the periods $\sigma_1, \sigma_2, \dots$ are equal or

commensurable. If this last condition is satisfied it seems probable that the quantum-equations of the system specified by equation (101) are

$$\int_0^{\sigma_s} 2T_s dt = \tau_s h, \quad (103)$$

which may, of course, be expressed in the alternative form

$$\int_{t=0}^{t=\sigma_s} p_s dq_s = \tau_s h. \quad (104)$$

Conditionally Periodic Systems.

72. In the more general system the energy, being of the general form

$$E = f(p_1, p_2 \dots q_1, q_2 \dots) \quad (105)$$

cannot be separated into a sum of terms in which each term depends only on one co-ordinate and its associated momentum. There will, however, in every special problem be a certain number of integrals of the classical equations of motion; let us suppose that in a special problem under consideration these are

$$\begin{aligned} \varphi_1(p_1, q_1, p_2, q_2 \dots) &= \alpha_1 \dots \\ \varphi_2(p_1, q_1, p_2, q_2 \dots) &= \alpha_2, \text{ etc.}, \quad (106) \end{aligned}$$

where $\alpha_1, \alpha_2, \dots$ are constants of integration which retain the same value throughout the motion of the system so long as this motion is in accordance with the classical dynamics.

In general the momentum p_s , being defined by

$$p_s = \frac{\partial E}{\partial q_s} \quad (107)$$

cannot be expressed as a function of q_s only. In special problems it may be possible to eliminate all co-ordinates and velocities other than p_s and q_s from equations (106) and (107), and obtain, for certain co-ordinates at least, equations of the type

$$p_s = f_s(q_s). \quad (108)$$

The equation $f_s(q_s) = 0$ may have any number of real roots. Each time the value of q_s reaches one of these roots p_s vanishes, so that in general the direction of the momentum p_s is reversed.

If the equation $f_s(q_s) = 0$ has no real roots, p_s retains the same sign throughout the motion, as, for example, in the case of motion in a straight line under no forces.

If the equation $f_s(q_s) = 0$ has only one real root Q , the motion will be one in which p_s will retain the same sign until q_s passes through the value $q_s = Q$, after which it will remain continually of the opposite sign, as, for example, in the case of the motion of a particle thrown up in opposition to gravity.

Except for these special cases, the equation $f_s(q_s) = 0$ will have at least two real roots, and if Q_1, Q_2 are two adjacent roots there will be a possible motion in which q_s will oscillate between the values Q_1, Q_2 . Such systems are called "conditionally periodic" systems. Each co-ordinate whose momentum can be expressed in the form (108) will oscillate between two fixed limits such as Q_1, Q_2 , just as though the co-ordinate belonged to a system possessing only one degree of freedom. An instance is provided by a particle describing an elliptic orbit about a centre of force

Since the energy of the system does not involve θ , the first equation of motion of the classical mechanics reduces simply to $p_1 = \text{constant}$, or

$$mr^2\dot{\theta} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (112)$$

In place of the second equation we may use the equation of energy, which may be written in the form

$$\frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2) - \frac{eE}{r} + W = 0$$

where W is the constant negative energy of the orbit, or again, using the values of the momenta given in equation (111)

$$\frac{1}{2m}\left(p_2^2 + \frac{p_1^2}{r^2}\right) - \frac{eE}{r} + W = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (113)$$

Since p_1 has been seen to be constant, this equation shows that p_2 is a function of r only. It is, moreover, a quadratic function of r , so that the value of r oscillates between two values r_1, r_2 which are the roots obtained by putting $p_2 = 0$ in equation (113). Physically, of course, these values of r_1 and r_2 are equal to $a(1 \pm \epsilon)$, where a is the semi-major-axis and ϵ the eccentricity of the orbit being described.

In accordance with the assumptions explained in §72, Sommerfeld takes the equations of restriction of the quantum-theory to be

$$\int p_1 d\theta = \tau_1 h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (114)$$

$$\int p_2 dr = \tau_2 h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (115)$$

where the limits of integration in equation (114) are from 0 to 2π , and in equation (115) are over the range from r_1 to r_2 and back again to r_1 .

The first equation simply requires that p_1 shall have a value of the form

$$p_1 = \frac{h}{2\pi} \tau_1$$

where τ is integral. On inserting this value for p_1 into equation (113), we find after integration that equation (115) assumes the form

$$\frac{\tau_1 h}{2\sqrt{(r_1 r_2)}} (\sqrt{r_1} - \sqrt{r_2})^2 = \tau_2 h.$$

On substituting for r_1 and r_2 , we obtain

$$W = \frac{2\tau^2 m e^2 E^2}{(\tau_1 + \tau_2)^2 h^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (116)$$

By a well-known formula the eccentricity ϵ of the orbit is given by

$$1 - \epsilon^2 = \frac{2W p_1^2}{m e^2 E^2},$$

or, inserting the value just found for W ,

$$1 - \epsilon^2 = \frac{\tau_1^2}{(\tau_1 + \tau_2)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (117)$$

In this formula τ_1 and τ_2 must be integral, so that the eccentricity ε is restricted to certain definite values. When $\tau_2=0$, $\varepsilon=0$, giving the circular orbits already considered; for all other values of τ_2 the eccentricity is finite, and we have elliptic orbits. If a , b are the semi-axes of the orbit $1-\varepsilon^2=b^2/a^2$, so that the values of the eccentricity permitted by equation (117) are those which make the ratio b/a commensurable, the value of this ratio being in fact $\tau_1/(\tau_1+\tau_2)$.

In formula (116) also, τ_1 and τ_2 must be integral, but the permissible values of W are seen to be the same as though $\tau_1+\tau_2$ was a single quantity restricted to integral values. Thus the values which are permitted to W when both τ_1 and τ_2 vary are precisely those which are permitted when τ_1 alone varies and $\tau_2=0$. The latter series of value of W being those which occur when the electron is restricted to circular orbits, are exactly those values of W which have already been seen to lead to the ordinary line spectra of hydrogen and helium.

It is now clear that the removal of the restriction that the electron-orbits must be circular leads to no new lines in the spectra of those elements; it does, however, lead to a somewhat different interpretation of the already discovered lines.

76. Consider as an instance the line H_α in the hydrogen spectrum. This is the first line of the Balmer series, and according to the simple theory of Chapter IV., is emitted whenever an electron falls from a circular orbit specified in our present notation by $\tau'_1=3$, $\tau'_2=0$ to a smaller circular orbit specified by $\tau_1=2$, $\tau_2=0$. According to the more complete theory just developed, this line must be emitted whenever the electron falls from any orbit whatever for which $\tau'_1+\tau'_2=3$ to an orbit for which $\tau_1+\tau_2=2$. The values $\tau'_1=0$ and $\tau_1=0$ are probably impossible since they would require the electron to pass through the nucleus, but after excluding them, there remain three sets of values of τ'_1 and τ'_2 for which $\tau'_1+\tau'_2=3$, and two sets of values of τ_1 and τ_2 for which $\tau_1+\tau_2=2$. Thus there are six possible events, any one of which results in the emission of the line H_α , and this line must now be regarded as the superposition of six separate lines, of which the line considered in Chapter IV. was only one.

The analysis which has suggested that the line H_α is formed by the exact coincidence of six separate spectral lines has been based upon certain assumptions which are only approximately true in fact. We have assumed in the first place that the mass m of the electron is negligible in comparison with the mass M of the nucleus. The error involved in this approximation can be removed by replacing m by $mM/(m+M)$ throughout, when the analysis becomes exact, precisely as in Chapter IV. We have also neglected the dependence of the mass of the electron on its velocity, and the error introduced here is not so easily corrected.

77. The necessary modifications of the preceding analysis, taking full account of the dependence of mass on velocity, have been given by Sommerfeld.* The mass m of an electron moving with velocity v is given by

$$m=m_0(1-\beta^2)^{-\frac{1}{2}}$$

where β is written for v/C , C being the velocity of light, and m_0 is the mass of the

* Ann. d. Physik, 51, p. 1 (1916), or "Atombau und Spektrallinien," Chap. 5. For an account in English see the English Translation (1923) of the latter, or J. H. Jeans, Dynamical Theory of Gases (3rd Edition), p. 420.

electron at rest. In place of being given by our former equations (110), the kinetic and potential energies are now given by

$$T = m_0 C^2 [(1 - \beta^2)^{-\frac{1}{2}} - 1], \quad V = -\frac{eE}{\gamma}. \quad (118)$$

As in the simpler case previously considered, the equations of motion have a first integral

$$m\gamma^2 \dot{\theta} = p_1$$

where p_1 is constant, this equation expressing the constancy of angular momentum. It is found that the second equation leads to the relation

$$\left[1 + \left(\frac{eE}{\gamma p_1 C}\right)^2 (1 - \varepsilon^2)\right] \left[1 - \frac{W}{m_0 C^2}\right]^2 = 1. \quad (119)$$

where W is the negative energy of the orbit, ε is the eccentricity, and γ is given by

$$\gamma^2 = 1 - \left(\frac{eE}{p_1 C}\right)^2$$

Sommerfeld now introduces the quantum-restrictions in the form already given in equations (114) and (115). Neglecting squares and higher powers of $(2\pi eE/hC)^2$, a small quantity of the order of 5×10^{-5} , we find that W can be expanded in the form

$$W = \frac{2\pi^2 m_0 e^2 E^2}{(\tau_1 + \tau_2)^2 h^2} \left[1 + \left(\frac{2\pi eE}{hC(\tau_1 + \tau_2)}\right)^2 \left(\frac{1}{4} + \frac{\tau_2}{\tau_1}\right)\right]. \quad (120)$$

The first term in this expression for W represents of course the value of W when the relativity correction is neglected—i.e., the value which W would have if C were infinite—and this leads to the spectrum already considered in which each line is the superposition of a number of separate lines.

When τ_2 is put equal to zero in equation (120) we obtain the values of W appropriate to circular orbits; the difference between these values and those previously obtained arising from the relativity-correction which is required on account of the velocity of the electron in its circular orbit. In the simpler case previously discussed, the removal of the restriction $\tau_2 = 0$ led to no new values for W . In the present case in which W has its full value given by equation (120) we find that the values of W corresponding to different values of τ_2 are all distinct; they differ from the values of W appropriate to circular orbits by small quantities which are proportional to τ_2/τ_1 . Sommerfeld believes that the frequency differences resulting from these small differences of energy exactly explain the observed fine structure of spectral lines.

The agreement between the predicted and observed frequencies in the fine-structure of lines cannot be claimed to be perfect. Some of the want of agreement must be attributed to the difficulties of measurement of the observed fine-structures of lines, but apart from this some lines which are predicted are not observed at all, suggesting that certain sets of values of τ_1 , τ_2 , τ'_1 , τ'_2 are prohibited altogether.

78. As an illustration of the kind of agreement observed, let us consider the case of the Balmer series of hydrogen. The line n of this series is emitted when-

ever an electron falls from an orbit τ'_1, τ'_2 for which $\tau'_1 + \tau'_2 = n$ to an orbit τ_1, τ_2 for which $\tau_1 + \tau_2 = 2$. The energy of the latter orbits, obtained by putting $e=E$ and $\tau_1 + \tau_2 = 2$ in equation (120), is

$$W = \frac{2\pi^2 m_0 e^4}{4h^2} \left[1 + \left(\frac{2\pi e^2}{2hC} \right)^2 \left(\frac{1}{4} + \frac{\tau_2}{\tau_1} \right) \right] \quad (121)$$

while the energy of the former, say W' , is similarly found to be

$$W' = \frac{2\pi^2 m_0 e^4}{n^2 h^2} \left[1 + \left(\frac{2\pi e^2}{nhC} \right)^2 \left(\frac{1}{4} + \frac{\tau'_2}{\tau'_1} \right) \right] \quad (122)$$

Thus, if ν_0 is the frequency of the line corresponding to circular orbits ($\tau'_2=0$; $\tau_2=0$), the frequency of the lines corresponding to non-circular orbits will be given by

$$\nu = \nu_0 + \frac{2\pi^2 m_0 e^4}{h^3} \left[\left(\frac{2\pi e^2}{n^2 hC} \right)^2 \frac{\tau'_2}{\tau'_1} - \left(\frac{2\pi e^2}{4hC} \right)^2 \frac{\tau_2}{\tau_1} \right] \quad (123)$$

The value $\tau_2=2$ is prohibited since this would make $\tau_1=0$, and would require the electron to pass through the nucleus. Thus the possible values for τ_2 and τ_1 are $\tau_2=1, \tau_1=1$ and $\tau_2=0, \tau_1=2$, giving $\tau_2/\tau_1=1$ and 0 respectively. Corresponding to any specified values of τ'_2 and τ'_1 there will be two values of ν with a frequency difference

$$\delta\nu = \frac{2\pi^2 m_0 e^4}{h^3} \left(\frac{2\pi e^2}{4hC} \right)^2 = 0.365,$$

and the complete line ought to consist of two similar structures separated by a frequency-difference 0.365. Since this is independent of n , it appears that the whole Balmer series may be supposed constituted of doublets of constant frequency difference 0.365, each constituent of these doublets showing its own fine structure.

Measurement of so small a separation is naturally difficult, and the observational results are far from accordant. For the separation of the doublet of $H_\alpha (n=3)$, Michelson has found $\delta\nu=0.32$, while Fabry and Buisson find 0.307, Merton and Nicholson* find 0.313, and Merton alone† by a more refined method 0.344. For H_β , again, Merton† has found $\delta\nu=0.372$, and for H_γ Michelson has found $\delta\nu=0.42$. Quite recently G. M. Shrum has measured the doublet separations of $H_\alpha, H_\beta, H_\gamma, H_\delta$ and H_ϵ respectively as 0.33, 0.36, 0.37, 0.36 and 0.35, with a probable error of 0.01 for H_β and of 0.02 for the other lines.‡ More accurate measurements can be made on the spectrum of positively charged helium, and from these Paschen has determined the frequency-difference as 0.3645 ± 0.0045 . There seems to be little room for doubt that the frequency-difference predicted by Sommerfeld, namely, 0.365, is very near to the truth.

We have given only one instance of the results of Sommerfeld's theory of fine-structure; a large number of other instances, with a full discussion as to their agreement with observation, will be found in his "Atombau und Spektrallinien," or its English translation "Atom Structure and Spectral Lines."

* Proc. Roy. Soc., 93, p. 27 (1917).

† Proc. Roy. Soc., 97, p. 318 (1920).

‡ British Assoc. (1923) Pres. Address to Section A.

The Stark and Zeeman Effects.

79. When the atom is placed in an electric field the superposed lines predicted by the simple theory of § 75 are separated out to an extent which, in the case of a strong field, may be much greater than the permanent separation produced by the relativity correction. This is the phenomenon known as the Stark effect. The amount of separation required by the quantum-dynamics, using the same equations of restriction as we have already employed, has been worked out by Epstein,* and has been found to be in excellent agreement with observation.†

A still wider separation can be produced by placing the atom in a powerful magnetic field, giving rise to the Zeeman effect. A theory of this in terms of quantum-dynamics has been given by Sommerfeld‡ and Debye,§ and this is found to show satisfactory agreement, as regards its general features, with observation. This theory employs quantum restrictions of the type we have had under consideration, except that the co-ordinates are supposed to be measured with reference to a system of axes in slow rotation. Recently W. Wilson|| has shown that the necessity for rotating axes can be avoided by taking the quantum restrictions in a slightly more general form, and the theory has been further developed by Mosharrafa.¶ Full details, with reference to both the Stark and the Zeeman effect, will be found in Sommerfeld's book.

BOHR'S PRINCIPLE OF CORRESPONDENCE.

80. We found in § 64 that the problems which had so far been discussed appeared to be governed by general laws, which we then expressed by the equations

$$2\tilde{T} = \tau h\nu \quad (\tau = 1, 2, 3, \dots) \quad (124)$$

$$\Delta W = \pm h\nu \quad (125)$$

We have proceeded as far as is at present profitable with the generalisation of equation (124), and now turn to a consideration of equation (125). Bohr has shown that this provisional equation admits of an especially interesting interpretation in the special case in which ΔW is so small that continuous differential analysis may legitimately be used.

Equation (124) has reference to a system describing a recurrent motion of period $\sigma = 1/\nu$, this motion being in accordance with the classical mechanics, so that if E is the total energy, expressed in the form (105),

$$\frac{dp_s}{dt} = -\frac{\partial E}{\partial q_s} \quad \text{and} \quad \frac{dq_s}{dt} = \frac{\partial E}{\partial p_s} \quad (126)$$

* Ann. d. Physik, 50, p. 489 (1916). For an account in English, see Sommerfeld's book, just referred to, or J. H. Jeans, "Dynamical Theory of Gases" (3rd Edition), p. 427.

† See also H. A. Kramers, Zeitschr. für Physik, 3, p. 199 (1920).

‡ Phys. Zeits., 17, p. 491 (1916).

§ Phys. Zeits., 17, p. 507 (1916).

|| Proc. Roy. Soc., 102, p. 478 (1923).

¶ Proc. Roy. Soc., 102, p. 529 (1923).

Following the classical mechanics, let us imagine that we pass to a slightly varied motion, of energy $E + \delta E$ and of period $\sigma + \delta\sigma$. Let us write

$$I = \frac{2T}{\nu} = 2 \int_0^\sigma T dt = \int_0^\sigma \Sigma p_s \dot{q}_s dt,$$

and suppose that in the varied motion I becomes $I + \delta I$. We then find by the ordinary calculus of variations

$$\begin{aligned} \delta I &= \int_0^\sigma \Sigma (\dot{q}_s \delta p_s + p_s \delta \dot{q}_s) dt + (\Sigma p_s \dot{q}_s)_{t=\sigma} \delta\sigma \\ &= \int_0^\sigma \Sigma (\dot{q}_s \delta p_s - \dot{p}_s \delta q_s) dt + (\Sigma p_s \delta q_s + \Sigma p_s \dot{q}_s \delta\sigma)_{t=\sigma} \end{aligned}$$

Since $\delta\sigma$ is given by the relation

$$\delta q_s + \dot{q}_s \delta\sigma = 0, \text{ when } t = \sigma$$

the last term is readily seen to vanish, while, by the use of equations (126) the first term gives

$$\delta I = \int_0^\sigma \Sigma \left(\frac{\partial E}{\partial p_s} \delta p_s + \frac{\partial E}{\partial q_s} \delta q_s \right) dt = \int_0^\sigma \delta E dt. \quad . \quad . \quad (127)$$

Since E and $E + \delta E$ remain constant throughout the two motions under consideration, δE will be independent of the time and we may write equation (127) in the form

$$\delta I = \sigma \delta E \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (128)$$

Suppose now that the system suddenly jumps from the motion of energy E to the adjacent motion of slightly different energy $E + \delta E$, the jump being supposed so slight that the calculus of variations may legitimately be applied. The frequency ν_R of the radiation which ought to be emitted according to equation (125) will be given by

$$\nu_R = \frac{\delta E}{h},$$

or again, by equation (128), putting ν for $1/\sigma$

$$\nu_R = \nu \frac{\delta I}{h} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (129)$$

Equation (124) which defines the possible motions is equivalent to

$$I = \tau h$$

We may suppose that

$$I + \delta I = \tau' h,$$

and now see that the condition that the differential calculus may be applicable is that τ' shall differ only infinitesimally from τ —i.e., that $\tau' - \tau$ shall be insignificant in comparison with τ . Since $\tau' - \tau$ must be an integer, this condition can only be satisfied if τ is very large, so that our analysis is applicable only to motions involving a very great number of quanta.

Putting $\delta I = (\tau' - \tau)h$, equation (129) becomes

$$\nu_R = (\tau' - \tau)\nu \quad (130)$$

showing that the frequency of the emitted radiation will be equal to $\tau' - \tau$ times the frequency of the oscillations of the system.

81. A simple illustration of this general theorem is provided by the hydrogen spectrum. If an electron jumps from an orbit possessing τ quanta to one possessing τ' quanta, the frequency of the emitted radiation according to the quantum-dynamics (*cf.* § 37) is

$$\nu_R = N \left(\frac{1}{\tau^2} - \frac{1}{\tau'^2} \right)$$

where N is Rydberg's constant. If τ and τ' are both large numbers, while $\tau' - \tau$ is small by comparison, this may be written

$$\nu_R = (\tau' - \tau) \frac{2N}{\tau^3} (131)$$

and it is readily seen (*cf.* equations (57)), that $\frac{2N}{\tau^3}$ is precisely the frequency of description of the original orbit, as is required by the theorem just proved.

82. The theorem is important, in that it appears to encourage hope as to the possibility of bridging the chasm between the classical mechanics and the quantum-dynamics. Under the classical mechanics, a system oscillating with a frequency ν will contain a certain number of charged electrons, each of which will oscillate with frequency ν , and the acceleration of these electrons will result in the emission of radiation. In general, any co-ordinates ξ of any electron can be analysed by Fourier's theorem into a series of harmonic terms in the form

$$\xi = \sum A_s \cos (2\pi s \nu t - \varepsilon_s) \quad (132)$$

($s=1, 2, 3,$), whence it is readily seen that the emitted radiation will be of frequencies

$$\nu, 2\nu, 3\nu$$

Now these are precisely the frequencies of radiation predicted by the quantum-equation (130).

Thus it appears that, in the limiting case of a system possessed of a very great number of quanta of energy, the spectrum predicted by the quantum-mechanics is identical, at least as regards its frequencies of vibration, with the spectrum predicted by the classical mechanics.

Bohr's "principle of correspondence" now asserts, as a hypothesis to be abandoned if it is found to be in disagreement with observation, that the intensity of lines in the quantum-spectrum will be similar to that in the spectrum predicted by the classical mechanics. Bohr further suggests that this "correspondence" in intensity persists, at any rate as an approximation, beyond the range in which the system possesses a very great number of energy-quanta—persists, that is to say, into regions in which the frequencies calculated from the quantum-theory do not coincide with those calculated from the classical mechanics.

83. A single instance, given by Bohr,* will illustrate the method of application of this principle. A simple oscillator of frequency ν_0 , can, in accordance with quantum-dynamics, have energies of amount given by

$$E = h\nu_0, 2h\nu_0, 3h\nu_0, \dots$$

If the system is free to jump from any one value of E to any smaller value, the frequencies of the emitted radiation, as calculated by the quantum-dynamics ($\Delta E = h\nu$), will be given by

$$\nu = \nu_0, 2\nu_0, 3\nu_0, \dots \quad (133)$$

Now if the system performs simply harmonic vibration, the co-ordinate of any moving part, when analysed by Fourier analysis after the manner of equation (132), will contain only one periodic term, and this will be of frequency ν_0 . Thus the classical dynamics predicts that the radiation emitted will be of the single frequency ν_0 .

The quantum-theory has, as we have seen, predicted radiation of frequencies $\nu_0, 2\nu_0, 3\nu_0, \dots$, but makes no prediction as to the intensities of these different radiations. The principle of correspondence, as used by Bohr, predicts that the intensities of the lines of frequencies $2\nu_0, 3\nu_0, \dots$ must all be zero, in order to "correspond" with the predictions of classical mechanics.

The nearest approach in nature to a simple harmonic oscillator is probably a diatomic molecule, and for many such molecules the frequency of the fundamental vibration is put in evidence by a pronounced absorption line in the infra-red. A significant confirmation of Bohr's principle is perhaps to be found in the fact that no absorption lines are observed of frequencies twice, three times, etc., the frequency of this line.

The "principle of correspondence" admits of many applications, a number of which show marked agreement with observation. Enough has perhaps been said to explain the general meaning of the principle; the student will find special applications elsewhere, particularly in the works of Bohr and Sommerfeld, to which reference has been made in the present chapter.

* "On the Quantum-Theory of Spectra," D. Kgl. Vidensk. Selsk. Skrifter, Part I., p. 16 (1918).

CHAPTER VIII.

THE PHYSICAL BASIS FOR THE QUANTUM-THEORY.

84. The foregoing chapters have given a summary of the principal pieces of experimental evidence bearing on the quantum-theory, and a statement of some of the mathematical analysis connected with it. It has by no means been found possible to represent the quantum-theory completely by a set of mathematical equations or of physical concepts. The general indications are that the most minute processes of nature are governed by a system of mechanical laws different from the classical laws, expressible by equations in which the quantum-constant h plays a prominent part. But these general equations remain unknown, and at most all that has so far been discovered is the form they assume in certain special cases.

It is, however, clear beyond all possibility of dispute that the quantum-theory has disclosed in nature a certain atomicity of a kind unsuspected by the older mechanics. In the form in which the quantum-theory was originally put forward by Planck this atomicity was in effect an atomicity of energy, although this conception was not exactly used by Planck. But the atomicity was dependent on the frequency of the vibrations in which the energy was stored, and seemed to have little or no meaning except in reference to absolutely monochromatic vibrations. It is more natural to suppose that the real atomicity, if it exists, is that of some other entity measured by h , or by some function of h and constants of nature. The constant h is physically of the dimensions of energy multiplied by time, or action. An attempt to imagine a universe in which action is atomic leads the mind into a state of hopeless confusion, but there is no reason for thinking that the ultimate physical atomicity is that of action. The classical equations of dynamics could be put in the form $\delta A = 0$, where A was the action, and was supposed capable of continuous variation. The motion of a system governed by the quantum-mechanics appears also to conform to the law $\delta A = 0$, at least throughout the greater part of the motion; but motion for which the values of A , calculated after the condition $\delta A = 0$ has been satisfied, are integral multiples of h , seems to have very special properties. Whether non-integral multiples of h are absolutely prohibited we do not know; it is perhaps most probable that the difference is one of degree only, motions characterised by integral values of h possessing a quality of permanence which is absent when h is non-integral. If so, the difference between motion with integral and non-integral values of h may perhaps be compared, very loosely, to that between stable and non-stable compounds in chemistry.

85. The quantity hV is of the physical dimensions of the square of an electric charge. In point of fact, $\frac{h}{2\pi} V$ is nearly equal to $(4\pi e)^2$, i.e., to the square of the strength of a tube of force binding two electrons. This suggests that the atomicity of h may be associated with the atomicity of e . The atomicity of e will not lead to the quantum-theory, for if it did the quantum-theory would have been fully developed long ago; but there is, perhaps, a hope that the two atomicities may be special aspects of some principle more general than either of them. It must be

remembered that the atomicity of e has never received a physical explanation; it is in no way implied in the classical equations of Maxwell, and no reason is known why an electron with a charge $\frac{1}{2}e$ should not exist. Any attempt to refer back the atomicity of e to the structure of a supposed ether simply discloses the fact that the fundamental equations of the ether are not yet fully known; it implies that if they were fully known they might be expected to contain the quantity e , and this is perhaps the same thing as saying that they would contain the quantity h . It may be that if these equations were fully known they would be seen to involve the quantum-theory. If $\frac{h}{2\pi} V$ is the same thing as $(4\pi e)^2$, an attempt to

give a physical explanation of the quantum-theory might be based on the atomicity and possible discrete existence of tubes of force of strength $4\pi e$, ideas with which we were first made familiar by the writings of Sir J. J. Thomson.* The principal evidence adduced by Sir J. J. Thomson in favour of a "corpuscular" or "atomic" structure of a field of radiation arose from a study of the ionisation of gases by X-rays. It was noticed that the ionisation was such as would be expected if the X-rays did not spread out in accordance with the undulatory theory of light, but moved with their energy concentrated in certain small, sharply defined regions. It is now understood that the ionisation produced by the X-rays is produced by the intermediary agency of β -rays, and this somewhat alters the problem. The question now becomes how the X-rays, if they are not concentrated, can produce β -rays as they do, and the problem really becomes identical with that of the photo-electric effect already discussed in Chapter V. But, before the identity of the two problems had become clear, a study of the photo-electric phenomenon had led Einstein to put forward the hypothesis of "light-quanta" (cf. § 47), a hypothesis in many respects similar to Thomson's earlier hypothesis of discrete tubes of force. Einstein's hypothesis required us to suppose that light travelled in separate highly-concentrated and indivisible "packets," each containing one quantum of energy.

86. This hypothesis has been unable to gain acceptance owing to its obvious conflict with the well-established principles of the undulatory theory of light. For instance, Prof. Lorentz says†:—

"Now it must, I think, be taken for granted that the quanta can have no individual and permanent existence in the ether, that they cannot be regarded as accumulations of energy in certain minute spaces flying about with the speed of light. This would be in contradiction with many well-known phenomena of interference and diffraction. It is clear that, if a beam of light consisted of separate quanta, which, of course, ought to be considered as mutually independent and unconnected, the bright and dark fringes to which it gives rise could never be sharper than those that would be produced by a single quantum. Hence, if by the use of a source of approximately monochromatic light, we succeed in obtaining distinct interference bands with a difference of phase of a great many, say some millions, of wave-lengths, we may conclude that each quantum contains a regular succession of as many waves, and that it extends therefore over a quite appreciable length in

* "Recent Researches in Electricity and Magnetism," Chapter 1 (1892), and later books.

† Discussion on "Radiation" at the Birmingham Meeting of the British Association (1913). See also a short article, also by Lorentz, "Die Hypothese der Lichtquanten," *Phys. Zeitschr.*, 11, p. 349 (1910).

the direction of propagation. Similarly, the superiority of a telescope with wide aperture over a smaller instrument, in so far as it consists in a greater sharpness of the image, can only be understood if each individual quantum can fill the whole object-glass. These considerations show that a quantum ought at all events to have a size that cannot be called very small. It may be added that, according to Maxwell's equations of the electro-magnetic field, an initial disturbance of equilibrium must always be propagated over a continually increasing space."

Certainly these objections to a theory of discrete "light-quanta" seem to be insuperable. It may be added that the question of the existence of indivisible quanta in the ether has been tested directly, or as directly as is possible, by experiment.

It is clear that if light occurred only in quanta, which did not themselves admit of being broken up, interference could only occur at a point at which two or more quanta existed simultaneously. If the light were sufficiently feeble the simultaneous occurrence of two quanta at any point ought to be a very rare occurrence, so that all phenomena, such as diffraction patterns, which depend on interference, ought to disappear as the quantity of light present is reduced. G. I. Taylor* has shown that this is not the case; he reduced the intensity of his light to such an extent that an exposure of 2,000 hours was necessary to obtain a photograph, and yet obtained photographs of diffraction patterns in which the alternation of light and dark appeared with undiminished sharpness. In Taylor's experiments the intensity of light was 10^{-16} erg per cubic centimetre, or about one light-quantum per 10,000 cubic cm., so that if the quanta had been concentrated nothing of the nature of a diffraction pattern could possibly have been observed. Quite recently a further experimental test by G. P. Thomson has led to the same conclusion.†

87. For these and other reasons it is now generally accepted that in regions in which matter is absent radiation is propagated in accordance with the classical laws of Maxwell. The fundamental law of quantum-dynamics, that radiant energy is emitted and absorbed only in complete quanta, is no longer interpreted as meaning that the ether can carry radiant energy only in complete quanta, but that matter can deliver or absorb radiant energy only by complete quanta. It is matter, and not ether or radiant energy, which proves to be different from what we had thought.

There is accordingly little reason for doubting that Maxwell's equations

$$\frac{1}{c} \frac{\partial X}{\partial t} = \frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z}, \text{ etc.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (134)$$

are true under the quantum-theory as they were under the old dynamics. But under the old dynamics X , Y , Z had a very precise meaning; they were components of a force, and an electron of charge e placed in the field would experience a mechanical force Xe , Ye , Ze . Under the quantum-dynamics this cannot be the true meaning of X , Y , Z , for if it were, an electron placed in a field of radiation would be absorbing energy otherwise than by complete quanta. Indeed, we have already seen in § 10 that the supposition that an electron in a field of radiation is acted upon by a force

* Proc. Camb. Phil. Soc., 15, p. 114 (1909).

† Proc. Roy. Soc., 104A, p. 115 (1923).

To obtain the classical mechanics exactly we put $\Delta W=0$. To obtain the quantum-mechanics we put $\Delta W=h\nu$. Our artificial chunks of energy become quanta, and in place of formula (136) we have that the number of quanta of energy transferred per unit time is proportional to $A^2/h\nu$. Or, since we do not contemplate the possibility of a single atom absorbing a whole succession of similar quanta, we slightly alter our statement and say that the probability of a quantum $h\nu$ of energy being transferred in unit time is proportional to $A^2/h\nu$.

According to Maxwell's equations $A^2/h\nu$ varies as $1/r^2$, so that the probability of an atom absorbing a quantum of energy varies inversely as the square of its distance from the source of radiation. We no longer think of a spherical wave as carrying with it a store of energy in each element of its wave-front, to be yielded up to whatever matter it encounters; we rather think of it as carrying with it a potentiality of yielding up energy to such matter as it encounters in a suitable state to receive this energy. The amount of energy which it may yield up remains always equal to $h\nu$, but the chance of its yielding this amount up falls off as $1/r^2$. The total "expectation" of the energy to be yielded up by the whole wave front, of area $4\pi r^2$, is accordingly independent of r . The conservation of energy now reappears, but merely as a statistical law, which is not necessarily true in every individual case, but has the same probability of truth as, for instance, the second law of thermodynamics. We are obviously far removed from the conception of radiation as energy which can be localised in space, and which moves about as directed by the law of the Poynting Flux; but the abandonment of this conception need cause no regrets.

90. On this or any other view of the meaning of radiation, there remains the outstanding difficulty of imagining a structure of matter such that an atom can absorb radiation only when it is offered in specified doses $h\nu_1, h\nu_2, \dots$, where $\nu_1, \nu_2 \dots$ are, so far as we know, perfectly definite frequencies.

In this connection we may notice that a free electron cannot accept a quantum of radiation under any circumstances whatever. For if an electron moving freely with a velocity u accepted a quantum $h\nu$ of energy from a field of radiation, its final velocity v would be given by

$$\frac{1}{2}mv^2 = \frac{1}{2}mu^2 + h\nu.$$

For an observer moving with a velocity v equal to the final velocity of the electron, this equation would reduce to

$$0 = \frac{1}{2}mu'^2 + h\nu'$$

so that the sum of two essentially positive quantities would have to be zero. Thus the simplest structure which can absorb a quantum of energy is a complete atom, and the same is obviously true with regard to emission.

In an atom we must suppose the electrons bound to the nucleus not only by its electrostatic force, but also by the more rigid bonds of the quantum-theory which, in some way at present totally unknown, compel that certain quantities associated with the orbit shall exist in complete quanta only. The simplest conception we can form of the absorption or emission of a quantum of energy is that these latter bonds are momentarily dissolved, that the whole atom is for the time being put, so to speak, into the melting pot, and that a new system, subject to new quantum-bonds, is in due course formed out of the old constituents endowed with

their new appropriate amount of energy. We are still very far indeed from being able to fill in the details of this picture, although we know that in the limiting case of radiation of very great wave-length, for which the emitting or absorbing electron must be very distant from the nucleus and the quantum-bonds so feeble that they may be disregarded altogether, the whole process becomes identical with that predicted by the classical mechanics.

91. If the point of view from which we have just been considering the question is a legitimate one, then the classical electrodynamics, and, of course, also the Newtonian mechanics, fall into place very naturally in the general scheme of nature. But as soon as we pass beyond the minute range covered by the classical electrodynamics and the Newtonian mechanics, the picture of this general scheme presented to us by the quantum-dynamics is strangely unexpected; we find—or at least we at present think we find—that nature consists of a series of more or less abrupt jumps, although just in that one particular corner of the picture which we have so far been able to explore with some thoroughness these jumps are so minute and so close together as to produce the illusion of continuous motion.

It is perhaps not altogether an idle question to inquire whether the surprise we all feel at the newly-discovered discontinuity, or apparent discontinuity, of nature is philosophically justifiable, or whether it arises merely from the inertia of our minds. A man who unrolls what he had thought, judging from one corner of it only, to be a crayon-drawing, and finds that it is a line-engraving, in which the illusion of continuity is limited to the one corner he first saw, is, no doubt, surprised, but he has only himself to thank, for his surprise arose merely from his having, in an unscientific frame of mind, generalised too hastily and assumed that the unseen would be in essence a repetition of the seen. Is or is not his surprise a fair analogy to the surprise which the progress of the quantum-theory has excited in us?

The supposed discontinuity may itself prove to be unreal; the “jumps” may ultimately be found to consist of a succession of continuous steps. To borrow an analogy from Poincaré: the first observer of a collision thought he was witnessing a discontinuous process, but we know to-day that what he saw was the result of changes which, although very rapid, were continuous. If there is a real difficulty in imagining discontinuity to be the ultimate rule of nature, we can escape this difficulty by imagining a sort of sub-universe such that the apparently discontinuous processes of the quantum-theory result from a rapid succession of continuous changes in this sub-universe. The conception of there being a definite “probability” of a spontaneous “jump” of a system from one state to another, a conception which is an essential feature of the view we have just been considering, may be thought to point rather in this direction. On the other hand, to some minds it may appear as likely that the ultimate scheme of nature will prove to be discontinuous as that it will be continuous. The circumstance that discontinuity was an unexpected solution of the problem ought not to prejudice us against the possibility of its being the final solution. For the history of science teaches that each great advance towards ultimate reality has shown this reality to lie in an entirely unexpected direction.

INDEX TO AUTHORS.

The numbers refer to the pages.

- | | |
|---------------------------------------------------------|------------------------------------|
| Balmer, 38, 39, 40, 41, 47, 71, 73. | Hamilton, 26. |
| Blake, 44, 61. | Hartmann, 48. |
| Bohr, 35-44, 47, 48, 49, 62, 66, 67, 69, 74,
76, 77. | Hertz, G., 48. |
| Boltzmann, 15, 65. | Hertz, H., 45. |
| Born, 56, 59, 60. | Horton, 49. |
| Brackett, 38. | Hull, 44. |
| Bragg, W. H., 57. | Hunt, 44. |
| Broglie, de, 50. | |
| Brown, 18. | Kármán, 56, 59, 60. |
| Bucherer, 38. | Keesom, 56, 61. |
| Buisson, 73. | Kelvin, 34. |
| Burgers, 65, 69. | Koref, 52. |
| | Kramers, 74. |
| Campbell, 63. | |
| Coblentz, 61. | Ladenburg, 45. |
| | Larmor, 9. |
| Darwin, 21. | Lenard, 45. |
| Davies, 49. | Lienhop, 45. |
| Davis, 49. | Lindemann, 52, 53, 57, 58, 59, 60. |
| De Broglie, 50. | Liouville, 15. |
| Debye, 53-58, 60, 69, 74. | Lorentz, 9, 13, 14, 33, 79. |
| Duane, 44, 61. | Lyman, 38, 39. |
| Dulong & Petit, 52. | |
| Dyson, 40. | Maxwell, 4, 33, 80, 82, 83, &c. |
| Ehrenfest, 65, 66. | Merton, 40, 73. |
| Einstein, from 22, continually quoted. | Michelson, 73. |
| Ellis, 50. | Millikan, 38, 41, 45, 46, 61. |
| Epstein, 41, 69, 74. | Moseley, 43. |
| Evans, 39. | Mosharaffa, 74. |
| Evershed, 40, 41. | |
| | Nernst, 52, 53, 57-60. |
| Fabry, 73. | Nicholson, 37, 40, 42, 66, 73. |
| Fourier, 77, 81. | |
| Fowler, A., 39, 41, 63. | Onnes, Kamerlingh, 56, 61. |
| Fowler, R. H., 21, 24. | Oxley, 60. |
| Franck, 48. | |
| Gerlach, 48. | Paschen, 38, 39, 41, 73. |
| Goucher, 49. | Pickering, 40. |
| Grüneisen, 60. | Planck, continually quoted. |
| | Pohl, 45. |

Poincaré, 7, 19, 24, 25, 28, 84.
Poynting, 83.
Pringsheim, 45.

Rau, 49.
Rayleigh, 8, 16, 17, 24.
Richardson, 13, 18.
Richter, 59.
Ritz, 63.
Rubens, 58.
Rutherford, 34.
Rydberg, 41, 61, 63, 76.

Sommerfeld, 44, 48, 49, 69-74, 77, 82.
Stark, 41, 74.

Stefan, 19.
Taylor, 80.
Thirring, 57, 59, 60.
Thomson, G. P., 80.
Thomson, J. J., 17, 18, 79.

Weyl, 14.
Wien, 19.
Wilson, W., 74.
Wood, R. W., 40, 48.
Wright, 41.

Zeeman, 33, 74.

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